A COMPARITIVE STUDY OF LOW-COST BIOMATERIALS FOR THE REMOVAL OF CHROMIUM (VI/III) FROM AQUEOUS SOLUTIONS

SYAM KUMAR PRABHAKARAN

NATIONAL UNIVERSITY OF SINGAPORE

2006

A COMPARITIVE STUDY OF LOW-COST BIOMATERIALS FOR THE REMOVAL OF CHROMIUM (VI/III) FROM AQUEOUS SOLUTIONS

SYAM KUMAR PRABHAKARAN

(B.Tech. (Hons.), NUS)

A THESIS SUBMITTED

FOR THE DEGREE OF MASTER OF ENGINEERING

DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING

NATIONAL UNIVERSITY OF SINGAPORE

2006

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my deepest gratitude and thanks to my supervisor Dr Rajasekhar Balasubramanian for his patience, guidance and support throughout the course of this project.

I would like to thank Dr. Karthik for his advices and the directions given to me constantly throughout the whole project, in addition my heartfelt gratitude goes to my groupmates and other university staff in ESE and Chemical department.

I also wish to thank all my collegues working in INVISTA and several former collegues from Regional Research Laboratory (RRL),Council of Scientific and Industrial Research (CSIR), Trivandrum for their guidance and help over the course of my studies

Last but not least, I would like to thank my wife, daughter and other family members and friends for their understanding and help during the entire period of my part-time studies.

ABSTRACT

The contamination of water by toxic heavy metals including chromium is a worldwide problem. The release of chromium into the environment has become a seroius health problem due to its toxicity. Increasingly strict discharge limits on chromium have accelerated the search for highly efficient yet economically attractive or alternative treatment methods for its removal. The use of low-cost and waste biomaterials as adsorbents of dissolved metal ions has shown potential to provide economic solutions to this global environmental problem.

Numerous studies on metal biosorption by brown seaweeds such as *Sargassum* have been reported. However the applicability of green seaweeds such as *Ulva* has not been extensively investigated yet for the removal of Cr(VI)/Cr(III), despite of its large abundance in the natural environment. In this study, laboratory scale investigations were conducted to compare the adsorption capabilities of *Ulva* with *Sargassum* for the removal of both Cr (VI) and Cr(III) from aqueous solutions. Various chemical pre-treatment methods were investigated for enhancing the adsorption capacity of both *Sargassum and Ulva* together with the use of other low cost waste biomaterials such as used tea and coffee dust.

The most influencing adsorption parameters such as initial pH, quantity of adsorbent, initial metal ion concentration and contact time were studied for *Sargassum, Ulva*, used tea and coffee dusts. The adsorption capacity of *Ulva* was lower compared to that of *Sargassum*. The removal of hexavalent chromium by seaweeds was observed as a process of adsorption together with reduction by different kinetic rates. *Ulva* biomass only

reduced less than 20% of the available Cr(VI) ions compared to a 100% reduction by *Sargassum*. However, *Ulva* and *Sargassum* have shown similar adsorption capacities for the removal of Cr(III) ions.

Experiments were conducted by using an external reducing agent to speed up the reduction process by which an enhancement in the adsorption of Cr(VI) by *Ulva* biomass could be achieved. Domestic wastes such as used tea and coffee dusts have been found to be a strong anit-oxidant and be able to reduce more than 90% Cr(VI) ions to Cr(III) ions within an hour. Adsorption experiments showed that used tea and coffee dusts are not only good anti-oxidants, but also potential adsorbents which have a better adsorption capacity than *Sargassum.*

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

C_0	-	Initial concentration
C_e	-	Equilibrium concentration (mg L^{-1})
C_{eq}	-	Final equilibrium concentration (mg L^{-1})
Cr	-	Chromium
C_t		Concentraion at any time
GAC	-	Granular activated carbon
k	-	Langmuir equilibrium constant, related to the affinity of the binding sites (L mg^{-1})
$[H]_{add}$	-	Concentration of added acid
K_F	-	Measure of adsorption capacity (Frendluich)
MCL	-	Maximum Contaminate Level
mg L^{-1}	-	Milligram per litre
1/n	-	Adsorption intensity
$[OH]_{add}$	-	Concentrations of added base
q_{eq}	-	Mass of adsorbate adsorbed per unit mass of adsorbent at final equilibrium concentration (mg g^{-1}). This is also described as the surface coverage.
q_{max}	-	Maximum adsorption capacity (mg g^{-1})
q	-	Amount of metal ions adsorbed at equilibrium (mg g^{-1})
psi	-	Pounds per Square Inch
V	-	Volume of sample
W	-	Weight of adsorbent in gram
Sargassum	-	*Sargassum* Sp.
Ulva	-	*Ulva Fasciata* Sp.

CHAPTER 1

INTRODUCTION

Heavy metals can be defined as metallic elements with an atomic weight greater than that of iron (55.8 g mol^{-1}), or as elements with a density greater than 5 g cm^3 (Schuurman and Marker, 1997). Concern about heavy metals is due primarily to their potential toxicity, persistence, and tendency to become concentrated in food chains (bioaccumulation).

Human exploitation of world's mineral resources and advances in industrialization has resulted in the presence of high levels of heavy metals in the environment. The presence of heavy metals in the environment causes adverse impacts on flora and fauna of the earth. Though many metallic elements are essential for nutritional and physiological requirements in living organisms, their overabundance can cause toxicity symptoms, or even death. There are a number of toxic heavy metals including chromium, whose increasing levels in the environment are of considerable concern. With the rapid development of various industries, wastes containing metals are discharged directly or indirectly into the environment. This trend has been increasing, especially in developing countries, and has brought serious environmental pollution and threatening to bio-life (Wang and Chan, 2006). Heavy metal pollution is arising from effluent discharges from a variety of industries such as mining, ore processing, metal processing operations, and industrial activities that make use of metallic compounds such as pigments, bio-acidic agents, tanning, electroplating textile dyeing etc.

The toxic characteristics of heavy metals can be summarized as follows: (1) the toxicity can last for a long time in nature; (2) some heavy metals such as chromium, arsenic, mercury etc.

could be transformed from relevant low toxic species into more toxic forms in a certain environment; (3) the bioaccumulation and bio-augmentation of heavy metals by food chain could affect normal physiological activity and endanger human life finally; (4) metals can only be transformed and changed in valence and species, but cannot be degraded by any methods including bio-treatment; (5) the toxicity of heavy metals occurs even in low concentration of about 1.0–10 mg L^{-1}. Some strong toxic metal ions, such as Hg, Cd and Cr, are very toxic even in lower concentration of 0.001–0.1 mg L^{-1} (Volesky, 1990a; Alkorta et al., 2004; Park et al., 2005). Due to their increasing application and the above immutable nature, the heavy metal pollution has naturally become one of the most serious environmental problems today.

Chromium is a metal found in natural deposits as ores, and also found in several other natural materials in its compound form. The greatest use of chromium is in metal alloys such as stainless steel; protective coatings on metal; magnetic tapes; and pigments for paints, cement, paper, rubber, composition floor covering and other materials and its soluble forms are used in wood preservatives (USEPA). Chromium may exist in several chemical forms and valence states in the environment. The most commonly occurring valence states are chromium metal (Cr(0)), trivalent Chromium (Cr(III)), and hexavalent Chromium (Cr(VI)). Chromium has been used in electroplating, leather tanning, metal finishing, and chromate preparation industries (Barnhart, 1997). Among its several oxidation states (e.g., di-, tri-, penta-, and hexa-), trivalent (Cr^{3+} and $CrOH^{2+}$) and hexavalent ($HCrO_4^-$ and $Cr_2O_7^{2-}$) species of chromium are mainly found in industrial effluents (Park et al., 2005). It is interesting that these two species of chromium exhibit very different toxicities and mobilities in the environment. Cr(III) is relatively insoluble at pH over 5 in aqueous systems and exhibits little or no toxicity (Anderson, 1997). In contrast, Cr(VI) is highly soluble and toxic, which is suspected to be a carcinogen and mutagen (Costa,

2003). The human health effects caused by Cr(VI) are lung cancer, respiratory irritation, dermatosis, dermatitis, and kidney and liver damage.

In the US alone, the production of the most water soluble forms of chromium, the chromate and dichromates, was in the range of 250,000 tons in a year. Though chromium occurs in nature mostly as chrome iron ore and is widely found in soils and plants, it is rarely found in natural waters. The two largest sources of chromium emission in the atmosphere are from the chemical manufacturing industry and combustion of natural gas, oil, and coal. When released to land, chromium compounds bound to soil are not likely to migrate to ground water. They are very persistent in water as sediments. Its concentrations in industrial waste waters range from 0.5 to 270,000 mg L^{-1}(Patterson 1985). There is a high potential for accumulation of chromium in aquatic life.

Chromium is also unique among regulated toxic elements in the environment in that different species of chromium, specifically Cr(III) and Cr(VI), are regulated in different ways based on their differing toxicities. Due to the severe toxicity of Cr(VI), the US EPA has set the Maximum Contaminate Level (MCL) for Cr(VI) in domestic water supplies to be 0.05 mg L^{-1}, while total Cr containing Cr(III), Cr(VI) and other species of chromium is regulated to be discharged below 2 mg L^{-1} (Baral and Engelken, 2002). In Singapore the Environmental Pollution Control Act restricts the release of Chromium to different water courses. The current limit of Cr in all forms (trivalent and hexavalent) is 1 mg L^{-1} for watercourse and 0.05 mg L^{-1} for controlled watercourse (NEA, Singapore).

Due to the increasing awareness of the deleterious ecological and health effects of toxic metals, a number of treatment methods have been developed over the years for their removal from

aqueous solutions. These methods mainly include reduction, ion exchange, electro-dialysis, electrochemical precipitation, evaporation, solvent extraction, reverse osmosis, chemical precipitation and adsorption (Patterson, 1985). However, these processes appear to be ineffective or extremely expensive, especially when the dissolved metals are at low concentrations (1 to 100 mg L^{-1}) (Volesky, 1990). Some of the disadvantages associated with the use of these methods include incomplete metal removal, high capital investment and operation costs, and loss of efficiency during regeneration process. Natural biomaterials such as seaweeds are available in large quantity. Certain waste products from industries, domestic, or agricultural operations also, have great potential to be used as inexpensive sorbents. The goal of the current study is to identify a suitable low cost biosorbent for the effective removal of Cr from aqueous solutions.

Motivation

There are several developments in the biosorption studies for the removal of Cr ions from various water sources. *Sargassum* was studied extensively for the removal of heavy metals including Cr. However the applicability of green seaweed biomass such as *Ulva* for metal removal has not been extensively investigated yet despite its large abundunce in the world's seashores. Chemical pre-treatments were studied for enhancing the adsorption capacities of biosorbents, but limited studies were conducted for the modification of *Ulva* biomass. Very few researchers have studied the effect of pre-treatment in *Ulva* in order to make this material as a comparable biosorbent with *Sargassum*. Several studies on the biosorption mechanisms of Cr(VI) adsorption proved that the mechanism is through the reduction and adsorption of Cr(III) ions onto the biosorbents, but few studies were conducted to make use of an external reducing

agent for instantaneous reduction of Cr(VI) to Cr(III) to enhance the adsorption mechanism using seaweeds (Katrochvil et al., 1998). Several studies have reported the effectiveness of biomaterials and bio-material based activated carbons for the adsorption of Cr ions by only analyzing Cr(VI) concentration in aqueous solutions resulting in incorrect elucidation of Cr biosorption. Cr(VI) was removed from aqueous solution systems by 'anionic adsorption'. However, it has been proved that Cr(VI) is easily reduced to Cr(III) by contact with organic materials under acidic conditions because of its high redox potential value (above +1.3V at standard condition). Thus, it is quite possible that the mechanism of Cr(VI) removal by biomaterials, or biomaterial-based activated carbons is not "anionic adsorption" but "adsorption-coupled reduction". It is therefore very important to analyze Cr(VI) and total Cr concentrations in aqueous solution during Cr adsorption studies. Several reports in the literature pointed out that plant biomass has the capability of reducing and retaining chromium species. However, no detailed investigations have been conducted to comparatively evaluate two different biomasses for the adsorption and reduction of Cr species from aqueous solutions.

Objectives

The main objective of this current research is to compare the efficiency of low cost biomaterials for the removal of Cr from aqueous solution. For that purpose, most commonly used brown algae (Sargassum sp..), less studied green algae (Ulva fasciata sp.), and waste coffee and tea dusts were evaluated. The additonal objective is to explore the possibility of improving the overall adsorption capacities of these different biomaterials by chemical pre-treatment and/or the use of chemicals or other biomaterials through enhancing the reduction of Cr(VI) ions during the adsorption process.

CHAPTER 2

LITERATURE REVIEW

This section provides background information related to the development of heavy metal removal processes and a review of the past studies done on the removal of Cr from aqueous solutions. In addition, the theories and factors influencing biosorption are presented. The purpose of this review is to discuss the current status of different treatment methods developed for the removal of Cr.

2.1 Conventional Chromium Removal Processes

Physicochemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies have been widely used to remove heavy metal ions from industrial wastewater. Precipitation is used as the treatment scheme to extract heavy metals from solutions by almost 75% of the plating companies (Cushnie, 1985). Precipitation of metals from contaminated water involves the conversion of soluble heavy metal salts to insoluble salts that will precipitate. Physical methods such as clarification (settling) and/or filtration will then remove the precipitate from the treated water. This process requires adjustment of pH, addition of a chemical precipitant, and flocculation. The most common precipitation methods in industries are hydroxide (or lime) precipitation, sulphide precipitation and sodium borohydride precipitation. In precipitation processes, a dissolved substance is forced to form a fine suspension of solid particles in order to effect a solid-liquid separation. It is dependent upon the theoretical solubility of the most soluble species formed and the separation of the solids

from the aqueous solution. Heavy metals are usually precipitated as the hydroxide by the addition of lime (calcium hydroxide) or potassium hydroxide or sodium hydroxide. These methods are relatively inexpensive and are useful for removing the bulk of the heavy-metal ions. However, they are not suitable where final clarification is required.

Ion exchange technologies have been successfully applied by metal finishing industries for several decades. The system that is most commonly used involves cation exchange resins to remove metal ions from a waste stream. Ion-exchange resins are insoluble polymers that have active ionogenic groups that are either permanently ionized, or capable of ionization or acceptance of protons to form the charged site. The resin interacts with mobile ions of opposite charge from the external solution. Ion exchange resins are capable of exchanging an H^+ ion for a cation in the waste stream, or in the case of anion resins, an OH^- ion for an anion in the waste stream. The resin is regenerated by an acid (cation resin), or a base (anion resin), when the exchangeable ions have been depleted. Ion exchange is a process in which ions are exchanged between a solution and an insoluble solid which is usually a resin. Several types of ion-exchange resins are commercially available and some of them exhibit a high specificity for certain heavy metals, however, a high capital expenditure is usually required in order to purchase and operate such a system. Current membrane processes have hindrance because of limited flow-rates, instability of the membranes in salt and acid conditions and fouling by inorganic and organic species (Volesky 1990 a ; Aderhold et al., 1996).

Reverse osmosis is an ex-situ separation process most commonly used in the desalination of the water. However, in the past decades a particular effort has been made for the application of reverse osmosis in the metal-finishing industry, with recovery of concentrated solutions of

metal salts and reuse of the water in cleaning. Reverse osmosis is aimed at separating water from ionic solutes (metal salts for example) and macromolecules. Reverse osmosis is a pressure driven reversal of the natural process of osmosis. In the osmosis process, water is transferred through a semipermeable membrane from the waterside of the membrane to the dilute solution side until an osmotic equilibrium is reached. In the reverse osmosis process, a hydraulic pressure (typically from 200 to 1200 psi) is applied to the salt solution side. This arrests, or reverses the flow of water through the membrane depending on whether the pressure equals or exceeds the osmotic pressure. Three types of semipermeable membrane materials can be used in the reverse osmosis units: cellulose acetate, hollow fibber polyamides, and polyether / amide on polysulfone membranes (thin film composite). Up to a few years ago, reverse osmosis membranes were made almost exclusively of cellulose acetate. But new thin-film composite has gained more attention recently. The performance of reverse osmosis depends on membrane composition and configuration, pressure, temperature and concentration of the feed water, the ionic charge and size of the specific treated ions.

Electrodialysis is a mass separation in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. More specifically, ionic materials are selectively transported within a stack of closely spaced ion exchange membranes. The driving force is provided by voltage from a rectifier and is imposed on electrodes at the two ends of the stack.

Evaporation is the use of an energy source to vaporize a liquid form from a solution, slurry, or sludge. In electroplating, nonvolatile metal salts are concentrated in the evaporating water and can be reused. Atmospheric evaporators operate at atmospheric pressure and release the

moisture to the environment. Vacuum evaporators are also used and vaporize water at lower temperatures. The Cart marker process (EPA, 1987) is an example of an atmospheric evaporator. Chromic acid additions were reduced by about 95% and the waste treatment by sodium bisulphate was eliminated. On the other hand, the cadmium platter process is an example of the vacuum evaporator and is used to recover cadmium salts from a cadmium cyanide plating system (EPA, 1987). Operating costs includes electrical power for the blower and pump equipment, and heat for evaporation (usually 626 watts per litre or 3.371 watts per gallon). Evaporation is an easy, maintenance-free, reliable and commonly applicable process. The main disadvantages are high-energy consumption and undesirable constituents in the recycled bath.

Carbon adsorption is a separation technology used to remove and recover certain inorganic compounds from single-phase fluid streams. Granular activated carbon (GAC) is used as the adsorbent. Activated carbons consist of amorphous forms of carbon that have been treated to increase the surface area/volume ratio of the carbon. The most widely used activated carbons are F-400 activated carbon from Calgon, which is made from bituminous material, and rice-hull activated carbon (RHAC). Some batch experiments have compared the heavy metal removal efficiency of the two types of GAC (Kim and Choi, 1998). The activated carbon F-400 was reported to effectively remove chromium and lead, but did not remove cadmium, while the rice-hull successfully removed cadmium and lead, but did not remove chromium. Adsorption processes are versatile in terms of apparatus and offer a relatively simple method for the removal of components, or impurities from liquid, or gaseous media. The absorbent has to have the capability to selectively condense or concentrate the targeted adsorbate (molecules, atoms, ions or particles) on its surface. Industrially important adsorbents include

activated carbon, silica gel, and alumina, which all have a porous surface structure and thus a high surface area. Accordingly, there is no requirement to use or maintain living organisms for the process. The process advantages of selecting non-viable biomasses have led to considerable research into the use of these systems for the removal of heavy-metal ions (Avery and Tobin, 1992; Orhan and Buyukgungor, 2000). The fact that such a broad range of biomasses have been shown to exhibit some affinity for heavy metals indicates that the use of cheap (or even waste) biomasses could be a future adsorbent in pollution control.

Chemical precipitation and electrochemical treatment are ineffective, especially when metal ion concentration in aqueous solution is as low as 1 to 100 mg L^{-1} (Volesky, 1990 a ; Volesky, 1990 b). They also produce large amount of sludge to be treated with great difficulties. Ion exchange, membrane technologies, and activated carbon adsorption process are extremely expensive, especially when treating a large amount of water and wastewater containing heavy metals in low concentration, so they cannot be used at large scale. In addition, they often create secondary problems since they give rise to metal bearing sludges.

Alternative technologies termed biosorption have been extensively studied in the last two decades, and are based on the metal-sequestering properties of certain natural biomasses, such as fungi, bacteria, and algae. These biosorbents possess metal-sequestering properties and can decrease the concentration of heavy metal ions in solution from ppm (parts per million) to ppt (parts per trillion) level. They can effectively sequester dissolved metal ions out of dilute complex solutions with high efficiency and quickly. Biological methods such as biosorption/ bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physicochemical methods (Kapoor and Viraraghavan, 1995).

Wide ranges of low cost adsorbents were studied for the removal of heavy metals. These include sorbents such as bark/tannin-rich materials, lignin, chitin/chitosan, dead biomass, seaweed/algae/alginate, xanthate, zeolite, clay, fly ash, iron-oxide-coated sand etc (Williams et al., 1996; Susan et al., 1999). Sorption depends heavily on experimental conditions such as pH, metal concentration, ligand concentration, competing ions, and particle size (Susan et al., 1999), so it is important to study these parameters during the biosorption experiments.

2.2 Biosorption

The biological method for metal remediation involves the use of living or non-living adsorbents. The use of living organisms is known as bioaccumulation, and this process has some practical difficulties. The industrial effluents usually contain high concentrations of toxic metals, and the pH conditions are usually extremely high or low. These conditions are not congenial for the survival of living cells. The living organisms have to be maintained in good physiological condition by providing a constant energy source. Finally, the acid and alkaline eluents used for metal recovery may kill the microorganisms and living cells. Therefore, this process is not feasible for all de-toxification procedures. On the other hand, biosorption by using dead biomass becomes an emerging technology, and it was recognized as a potential alternative for recovery of heavy metals from industrial waste streams.

Biosorption is based on the following mechanisms: physical adsorption, ion exchange, complexation, and precipitation. Biosorption may not necessarily consist of a single mechanism. In many sorption processes, more than one of these mechanisms take place, and it is difficult to distinguish between the single steps (Lacher and Smith, 2002). The major advantages of biosorption include: (i) low cost, (ii) high efficiency of heavy metal removal

from diluted solutions, (iii) regeneration of the biosorbent, and (iv) the possibility of metal recovery. In the last several years considerable attention has been focused on biosorption of metal ions from aqueous effluents (Holan and Volesky, 1995).

Recent investigations by various groups have shown that selected species of seaweeds possess impressive sorption capacities for a wide range of heavy metal ions. Seaweeds are a widely available source of biomass as over two million tones are either harvested from the oceans, or cultured annually for food or phycocolloid production, especially in the Asia-Pacific region (Zemke and Ohno, 1999). Among the different biological substrates tested in biosorption studies, algal biomass has received considerable attention due to the cost saving, low sensitivity to environmental and impurity factors, the possible contaminant recovery from the biomaterial, and its elevated adsorption capacity. This applies to *Sargassum* and *Ulva*, which are available in large quantities in littoral zones and therefore, an inexpensive sorbent material.

Among the most promising biomaterials studied, seaweeds are found to be very efficient and bind a variety of metals (Holan and Volesky, 1995). Many types of biomass have been reported to have high uptake capacities for heavy metals, including Cr. Among these materials, some species of brown marine algae exhibit much higher uptake values than other types of biomass, higher than activated carbon and comparable to those of synthetic ion exchange resins. The presence of key functional groups on the algal cell walls is responsible for their outstanding metal-sorbing properties (Davis et al., 2003). Marine algae, popularly known as seaweeds, are biological resources and are available in large quantities in many parts of the world. The algal cell wall of marine algae contains a high proportion of alginate constituting 14–40% of the dry

weight of the biomass. Alginic acid is a polymer composed of un-branched chains of 1, 4-linked h-d-mannuronic and a-l-guluronic acids (Percival and McDowell, 1967).

2.3 Use of Seaweed as Biosorbent

Among the various seaweeds investigated, *Sargassum* Sp. possesses superior metal binding capacity (Holan and Volesky, 1995). *Sargassum* is a type of brown algae, and it is abundantly found along the coast of beaches. The cell wall constituents and the porosity of the cell wall play an important role in biosorbent metal uptake and binding (Volesky, 1990a). Different types of algae have different cell constituents, composition and structure. *Sargassum* contains high amount of alginate within its cellular structures. These alginates are common to brown seaweeds, and the carboxyl groups of uronic acids (guluronic, mannuronic, glucuronic) in the alginate are the dominating binding groups (Volesky, 2003a). The alginate matrix is in a gel phase and hence makes it easily penetrable for small metallic cations; this makes it a suitable biosorbent with a high sorption capacity (Siegel and Siegel, 1973).

Sargassum species are found throughout tropical areas of the world and are often the most obvious macrophyte in near-shore areas where *Sargassum* beds often occur near coral reefs. *Sargassum* constitutes about 10 ± 40% of the brown algal dry weight (Percival and McDowell 1967), between 17% and 45% alginate contents (Chapman 1980; Fourest and Volesky 1996) which corresponds to 0.85 ± 0.25 mequiv/g of carboxyl groups per dry weight. Brown algae also contain about 5 ± 20% of the sulfated matrix polysaccharide fucoidan (Chapman, 1980) about 40% of which are sulfate esters. Fourest and Volesky (1996) reported that 0.27 mequiv/g of sulfate groups are found in *Sargassum* seaweed.

Ulva is thalli thin, sheet-like, consisting of wide blades, 10 - 15 cm wide at base, tapering upward to less that 2.5 cm wide at tip, up to 1 meter long. The color of *Ulva* is normally bright grass green to dark green, gold at margins when reproductive, and may be colorless when stressed. *Ulva fasciata sp.*, or "sea lettuce", is commonly found in areas where nutrients are high and wave forces are low. It is tolerant of stressful conditions, and its presence often indicates freshwater input or pollution.

Ulva species are early successional algae, quickly taking over new substrate on boulders that are cleared by storm disturbance. *U. fasciata* and *Enteromorpha flexuosa* are generally the first macro-algae to colonize newly opened substrate in inter tidal areas with high nutrients. The alga's reproductive success is partly due to the reproductive cells' photosynthetic ability. Reproductive cells of *Ulva fasciata* have similar photosynthetic rates to adult vegetative cells, with higher respiration rates. The growth of dense green seaweed mats of *Ulva* sp. is an increasing problem in estuaries and coasts worldwide, the enormous amount of *Ulva* biomass thus becomes a troublesome waste disposal problem (Suzuki et al., 2005).

However, the applicability of green seaweed biomass such as *Ulva* for metal removal has not been extensively investigated yet despite its large abundance in the world's shorelines (Morand and Birand, 1996; Valiela et al., 1997). Many of the studies to date on metal biosorption by seaweeds have largely been restricted to various species of brown seaweeds. On the other hand, green and red seaweed species have not been evaluated comprehensively. Lee et al., (2000) screened 48 species of brown, green, and red seaweeds for their uptake capacities of Cr (VI) while Jalali (2002) reported the biosorption of lead by eight species of brown, green, and red seaweeds. Karthikeyan et al., (2006) investigated the adsorption properties of *Ulva fasciata* and

Sargassum sp. for the biosorption of Cu (II) and reported comparable adsorption parameters between *Ulva* and *Sargassum.*

2.4 Biosorption Enhancement by Chemical pre-treatment

The biosorptive removal of metal ions from aqueous solution mainly depends on chemical mechanisms involving the interactions of metal ions with specific groups associated with the cell wall of microorganisms. Extensive studies carried out on biosorption reported its dependence on solution chemistry, ionic competition by other metals, influence of pH, ionic concentrations and kinetics (Fourest and Roux, 1992; Raji and Anirudhan, 1998).

The role of -COOH groups of cell wall alginate in ascophyllum nodosum and the involvement of ion exchange mechanisms were reported for the biosorption of cobalt by Kuyucak and Volesky (1989). Chemical coordination of Cu^{2+} ions to the dead biomass of *Ganoderman licidum* was investigated by Muraleedharan et al., (1994). The beneficial effects of chemically modified biosorbents have been discussed by Xie et al., (1996). However these reports have not established the specific sites responsible for metal binding. Ashkenazy et al., (1997) reported the involvement of negatively charged -COOH groups of the yeast biomass in Pb^{2+} biosoprtion through FTIR spectroscopic analysis.

Several studies reported the use of pre-treated biomass for metal removal and suggested the enhancement of sorption ability of the biosorbent. Treatment of *Saccharomyces cerevisiae* biomass with acid, alkali, and formaldehyde resulted in enhancement of cadmium and zinc uptake (Ting and Teo, 1994; Kim et al., 1995) reported that the lead biosorption capacity of microbial cell wall could be enhanced to nearly five fold by modification with chelating groups

such as hydroxamic acid, phosphates, and zanthic acid.

2.5 Biosorption for the Removal of Chromium

The brown marine algae *Sargassum sp*. and *Padina* sp., were used for the removal of cations (Cd^{2+} and Cr^{3+}) and anoins ($Cr_2O_7^{2-}$) by Ping et al., (2004). Their studies concluded that the removal of chromate is much slower for both algae. It took 360 minutes to achieve 90% of the maximum uptake capacity (reported q_{max} was 0.61 mmol g^{-1} of Cr(VI) and 0.79 mmol g^{-1} for Cr(III) ions by *Sargassum*). They also conducted X-ray photoelectron spectroscopy to study the oxidation state of Cr present on the biomass surface and found that the majority of the adsorbed Cr was in the trivalent form. The mechanism of Cr(VI) removal was considered to be via adsorption/reduction processes. The adsorption study of Cr(VI) using various biosorbents also revealed that the Cr(VI) ions in the solution were first reduced to Cr(III) ions and the Cr(III) ions were then adsorbed on the surface of the biosorbents. Reduction of Cr (VI) can occur under a variety of conditions, even in the presence of oxygen, if a suitable reducing agent is available (Anderson et al., 1994).

2.6 Reduction of Cr(VI) to Cr(III)

The conventional methods for removing Cr(VI) ions from wastewater are based on chemical reduction, using chemical reductants, such as $FeSO_4$.$7H_2O$, Na_2SO_3, $NaHSO_3$, and $Na_2S_2O_5$, followed by a chemical precipitation process (Kurniawan et al., 2006). Park et al., (2004) reported that when Cr(VI) containing synthetic wastewater was brought into contact with the biomass, the Cr(VI) was completely reduced to Cr(III), which appeared in the solution phase, or to be partly bound to the biomass. However, this process required a high amount of

chemicals for reduction and precipitation and also produced a voluminous toxic sludge which may pose disposal problems (Ramos et al., 1994). The problems associated with on-site regeneration and re-use have made the process less attractive. However, the results which have been reported in the literature are variable, particularly in terms of the optimal pH for Cr adsorption.

It has been proven that, when Cr(VI) comes in contact with organic substances or reducing agents, especially in an acidic medium, Cr(VI) is easily or spontaneously reduced to Cr(III), because Cr(VI) has high redox potential value (above +1.3 V under standard conditions)(Park et. al., 2006 b). Several studies did not consider the reduction mechanism in the Cr (VI) adsorption process, the adsorption capacity was simply evaluated by the difference between the initial and final concentrations of Cr (VI), or total Cr in aqueous solution. In most studies, only Cr (VI) in aqueous solution was analyzed using the colorimetrical method, the pink-colored complex that is formed from 1, 5-diphenylcarbazide and Cr (VI) in acidic solution can be spectrophotometrically analyzed at 540 nm. X-ray absorption spectroscopy (XAS), or X-ray photoelectron spectroscopy (XPS) has been used to determine the oxidation state of Cr ions. Torresdey et al (2000) reported that Cr (VI) could be bound to oat byproduct, but easily reduced to Cr (III) by positively charged functional groups, and subsequently adsorbed by available carboxyl groups. Because the reduction of toxic Cr(VI) leads to the formation of stable, nontoxic Cr(III), it is important to study how this reduction may be implemented to achieve detoxification and therefore environmental cleanup. Reduction of Cr(VI) can be accomplished abiotically by reactions with aqueous ions, by electron transfer at mineral surfaces, by reduction with humic substances and other organic molecules, and by lyophilized plant tissue (Wittbrodt et al., 1996).

2.7 Use of low cost biomaterials as reducing agent and adsorbent

Insoluble cell walls of tea leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins, and structural proteins (Tee and Khan, 1988). In other words, one-third of the total dry matter in tea leaves should have good potential as metal scavengers from solutions and wastewaters since the above constituents contain functional groups. Tea extracts are powerful antioxidants, mainly owing to the presence of (+) catechin, (−) epicatechin, (−) epigallocatechin, (−) epigallocatechin gallate and (−) epicatechin gallate (Farhosh et al., 2005). The solid wastes of commercially available tea leaves were found to be good sorbents of metal ions, especially Pb(II), Cd(II), and Zn(II) ions, the extent of adsorption depends on pH, ionic strength, metal concentration, substrate concentration, and the presence of interfering ions and surfactants (Tee and Khan, 1988).

The amount of dry tea produced from 100 kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4 kg of dry tea material is wasted. The tea waste has long been used as fuel in the tea-manufacturing processes (4410 kcal/kg) or as fertiliser in local tea cultivation after composting (Cay et al., 2004). There is a significant amount of tea dust wasted during the consumer usage.

The actual mechanisms of adsorption and reduction of higher oxidation state metal ions such as Cr(VI) are not known well. It is thought that ion exchange, complexation, and electrostatic interactions play an important role in the whole adsorption process of tea waste. Ion exchange mechanism considers the well-known model of metal binding and proton releasing reaction. Experimental pH measurements of the original metal solutions, before and after adding tea waste, showed that ion exchange is only a part of the whole adsorption process since the ratio

of the theoretical and experimental pH changes deviated considerably from unity.

CHAPTER 3

MATERIALS AND METHODS

3.1 Reagents Used

3.1.1 Standard Solutions of Chromium

Chromium (VI) solution:

7.0718 g of potassium dichromate ($K_2Cr_2O_7$) was dissolved in deionized water to prepare a stock Cr (VI) solution of 2500 mg L.$^{-1}$ Different concentrations ranging from 5 – 500 mg L^{-1} were prepared for the biosorption experiments from the 2500 mg L^{-1} Cr (VI) stock solution, potassium dichromate GR ($K_2Cr_2O_7$), Merck (1.04864.0500), Assay 99.9% .

Chromium (III) Solution**:**

24.0101 g of potassium chromium sulfate 12-hydrate ($KCr(SO_4)_2 12H_2O$) was dissolved in deionized water to prepare a stock Cr (III)solution of 2500 mg L^{-1}. Different concentrations ranging from 5 - 500 mg L^{-1} used for the biosorption experiments were prepared from the 2500 mg L^{-1} Cr (VI) stock solution.

3.1.2 0.1 N Hydrochloric Acid : 1 mL of laboratory grade hydrochloric acid (HCl, Merck (1.00317.2500), assay 37%) was diluted to 120 mL using ultrapure water.

3.1.3 0.1 N Sodium Hydorxide : 0.4 g of NaOH salt (JT Baker (3722-19), assay 98.6%) was dissolved in ultrapure water to 100 mL in a volumetric flask.

3.1.4 10% (v/v) Sulfuric acid : 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4 was diluted to 100 mL with reagent water.

3.1.5 Diphenylcarbazide solution: 250 mg 1,5-diphenylcarbazide was dissolved in 50 mL acetone, and stored in a brown bottle. The solution was discarded when it became discolored.

3.1.6 500 ppm Ferrous Ammonium Sulfate : 0.350 g of ferrous ammonium sulfate hexa hydrate salt ($(NH_4)_2Fe(SO_4).6H_2O$), Merck (1.03792.0500, Assay 99%) was diluted to 100 mL using ultrapure water.

3.1.7 10% Hydroxylamine Hydrochloride : 10 g of hydroxylamine hydrochloride salts ($(NH_2OH.HCl)$, JT Baker (2195-01), Assay 96.1%) was diluted in 100 mL ultrapure water.

3.1.8 1% Ascorbic Acid solution : 1 g of ascorbic acid salt ($(C_6H_8O_6)$, BDH (103033E)) was dissolved in 100 mL of ultrapure water

3.1.9 1 N Sodium Hydroxide Solution: 1 molar solution of NaOH (assay 98.6%) was prepared by dissolving 4 g of sodium hydroxide pellettes into ultrapure water.

3.1.10 Formaldehyde (1:2 Vol% of HCHO solution): 37% formaldehyde was diluted in the ratio of 1:2 by using deionized water (30 ml Formaldehyde mixed with 60 ml of ultrapure water).

3.1.11 50% (v/v) Acetone solution : Acetone was diluted with ultrapure water in 1:1 ratio.

3.2 Biomaterials

Brown seaweed (*Sargassum*.sp) and green seaweed (*Ulva fasciata*.sp) were used as biosorbents for the initial study. Several biomaterials were used to evaluate their reducing capacities and removal efficiency for Cr. The term 'raw biomass' refers to the seaweed biomass which was first washed several times in the laboratory using distilled water. Subsequently, the wet

biomass was dried in the oven at 50^0C.

3.2.1 Sargassum

Fresh biomass of *Sargassum sp.* was collected from the beaches of Labrador Park in Singapore. It was rinsed with deionized water and dried under the sun. The dried biomass was then ground in a blender, and sieved to obtain a particle size range of 500 -850 microns using a standard test sieve. Care was taken to make sure that no metallic containers were used during the cleaning and storage of the algal sample.

3.2.2 Ulva

The green colored marine algae *Ulva fasciata sp.,* used in the present study, was collected from the coastal belt of Thiruvananthapuram, Kerala, India. The collected algae was washed with DI water several times to remove the impurities. The washing process was continued till the wash water contains no dirt. The washed algae were then completely dried in sunlight for 10 days. The dried product was then cut into small pieces, and was powdered using a domestic grinder, and seived using a stanard testing seive to a particle size of 500 – 800 microns.

3.2.3 Modified Biomass

The modified biomass was prepared in the laboratory by contacting the seaweed with different chemicals. In all modification process a standard methodology was followed. 5 g of biomass was mixed with 100 mL of prepared chemical reagent and agitated at 120 rpm for 24 hours. The biomass was separated by filtration. During the filtration process, the pre-treated biomass was washed several times using ultra-pure water. This biomass was dried in an oven at 60^0C for 24 hours. The following chemicals were used for the pre-treatment of *Sargassum* and *Ulva* biomass.

1. Alkali Extraction: 0.1 N NaOH solution
2. Acid Extraction: 0.1 N HCl solution
3. Formaldehyde: Diluted 37% HCHO in 1:2 ratio by ultrapure water
4. Acetone: 50% (by vol) acetone solution

3.2.4 Tea and Coffee Dust

Waste Tea and coffee dusts (used tea and coffe dust) obtained from home and coffee shops were used in this study. Different types of tea and coffe dust were tested, and there were no difference observed for various brands of tea or coffee dust. Used tea and coffee wastes were dried under the sun, and this dried powder was directly used as adsorbents. Used tea and coffee dust is a domestic waste material, ,adsorbent. Almost 80-90% of the original quanity of these powder became waste after preparing tea and coffee; this waste can be effectively used for the adsorption of heavy metals.

3.3 Biosorption Studies

The uptake of heavy metal ions can take place by entrapment in the cellular structure and subsequent sorption onto the binding sites present in the cellular structure. This method of uptake is independent of the biological metabolic cycle and is known as ‘‘biosorption’’ or ‘‘passive uptake’’. The heavy metal uptake can also involve its passage into the cell across the cell membrane through the cell metabolic cycle. This mode of metal capture is referred to as ‘‘active uptake’’ (Kapoor et al., 1999). Therefore biosorption is a process that uses any biomass to sorb ions from aqueous solutions. If one considers that nonviable biomass is not biologically active, its metal uptake can be regarded as a passive adsorption process and, thus, be correlated with mathematical sorption models as the Langmuir and Freundlich equations.

Therefore, in the present work, the adsorption of Cr ions by *Sargassum* and *Ulva* was studied by investigating the influence of different experimental parameters on Cr, such as sorption time, initial pH, and initial Cr concentration.

All batch biosoprtion experiments were performed by adding 100 mg of dried biomass (*Sargassum and Ulva)* to 100 mL of Cr solution in 250 mL Erlenmeyer flasks. The flasks were agitated at 150 rpm for 3 - 6 hours. The experimements were conducted at room temperature. To avoid hydroxide precipitation at high pH, 0.5 g or more amount of ammonium acetate was added (Gong et al., 2005) to the solution before adjusting the pH. Algal mass quantity was fixed at 0.1 g L^{-1} as the optimum concentration. For kinetic experiments, 1 L of ionic solution was used to reduce the impact of the reduction in the volume of solution due to frequent sampling. After the prescribed adsorption period with agitation on the orbital shaker, the solution and the metal-loaded biomass were passed through a Whatman No. 1 filter paper. Metal-free and biosorbent-free blanks were used as controls. The filtrate was collected, and the residual total Cr and Cr(VI) were determined separately by ICP-OES (Optima 3000, Perkin Elmer, USA) and UV Spectrophotometer (Model U-2800). The Cr(III) concentrations were calcualted by taking the difference between total Cr and Cr(VI) concentration in the solution.

The initial concentration, C_0 (mg L^{-1}) and metal concentration at any time, C_t (mg L^{-1}) were determined by ICP-OES and the metal uptake q (mg metal ion g^{-1} of biosorbent) was calculated from the mass balance as follows:

$$q = \frac{(C_0 - C_t).V}{w.1000} \qquad \text{Eq. No 1}$$

where V is the volume of solution in ml and w the mass of sorbent in g. Preliminary

experiments had shown that Cr adsorption losses to the flask walls and to the filter paper were negligible. The experimental data for Cr(III) and Cr(VI) adsorption systems were correlated by both linearized Langmuir and Freundlich equations.

3.3.1 Effect of Solution pH: The biosorption of Cr (VI) and Cr (III) was studied for solution pH ranging from 1 – 10, 0.1 N HCl or NaOH solutions were used to adjust pH values. All pH measurements were taken using a laboratory pH meter (Denver instrument, Model 25).

3.3.2 Effect of Initial Concentration: The initial concentrations of CrCr (VI) and (III) ions were varied from 5 to 500 mg L^{-1}. 0.1g of each adsorbent was contacted with 100 ml of different concentrations of both Cr(VI) and Cr(III) ions solutions. Samples were drawn at regular intervals for the detection of unbound Cr (VI) ions.

3.3.3 Kinetics of Chromium Adsorption: 1 g of each biosorbent was contacted with Cr (VI) and Cr (III) solutions (25 mg L^{-1}) for different periods of time. 1 g of different biosorbents was added to 1 L of ionic solution, and the solution was mixed using a laboratory magnetic stirrer (Fisher Scientific). 5 mL of samples was taken in frequent intervals using a micropippette, and filtered through No 1 whatman filter paper. The samples were collected, and analyzed for up to 24 hours. More frequent samples were collected at the initial stage of the experiment.

The effects of particle size, temperature, and the effect of turbulence/agitation during the adsorption of Cr(VI) and (III) ions were not studied as part of this project. All experiments were conducted at room temperature, since previous studies indicated that temperature fluctuations between 10 and 35°C did not affect the biosorption performance (Aderhold et al., 1996). All experiments were conducted in replicates (n = 4), and the average readings were

taken for reporting purpose.

3.4 Analytical Methods

Two different analyses were condcuted for the determination of Cr ions in the solution; (1) total Cr (i.e., with consideration as to its oxidation state), and (2) Cr(VI) (Cr III can be inferred from the difference between the two Cr concentrations). The analysis for total Cr is less complex and controversial than the analysis for Cr (VI).

3.4.1 Total Chromium Concentration

The overall concentration of Cr in aqueous samples i.e the sum of the concentration of Cr (VI) and Cr (III) under the given pH and sample concentration was determined using an Inductively Coupled Plasma – Optical Emission Spectrophotometer (ICP – OES, Perkin Elmer model 3100) at a wavelength of 357.9 nm. Five point calibrations in the concentration range between 0 and 200 mg L^{-1} were used with ICP-OES. The standard solutions (0, 5, 10, 25, and 200 mg L^{-1}) were prepared from 2500 mg L^{-1} Cr(VI) stock solution prepared separately. The instrument was verified using another set of verification standards prepared from 2500 ppm Cr(III) standard solution. The concentration of trivalent Cr (Cr (III)) was determined as the difference between the total concentration of Cr determined by the ICP-OES and the concentration of hexavalent (Cr(VI)) measured in the spectrophotometer.

The samples were then left shaking overnight using a laboratory orbital shaker (Model (DK-08010), Daiki science Co. Ltd) for complete equilibration and the final pH was recorded. Initial and final metal concentrations in the experiments involving heavy metal binding were measured by ICE-OES.

3.4.2 Analysis of Chromium (VI) ions

The concentration of the residual Cr(VI) ions in the solution was determined spectrophotometrically at 540 nm (EPA Method 7196). Dissolved hexavalent Cr, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A redviolet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of Cr being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance was measured photometrically at 540 nm. The Cr reaction with diphenylcarbazide is usually free from interferences The known interference metals ions for this method (hexavalent molybdenium, mercury, vanadium and iron (EPA method 7196)) were not present in the synthetically prepared experimental solution. A laboratory spectrophotometer providing a light path of 1 cm was used to measure the Cr (VI) concentration at 540 nm. Since the stability of Cr(VI) in extracts is not completely understood, the analysis was carried out soon after preparing the solutions.

3.4.2.1 Calibration of the unit: A wide range of known concentration Cr concentrations (0.3125, 0.625, 1.25 mg L^{-1}) of calibration standards were prepared by diluting 0.25, 0.5, and 1 ml of 25 ppm Cr (VI) solution in cleaned glass vials. 2 ml of H_2SO_4 (0.1M H_2SO_4 to reduce the pH of the solution to below 2) and 0.5 ml of diphenylcarbazide were added to each vial. Ultrapure water was used to top-up the total volume of the solution to 20 ml. All volumetric measurements were carried out by using a micropipette with different volumes (0.5 ml, 1.0 ml, and 5 ml). Several calibrations carried out in different days of the experiments proved that the absorbance was same for the same conectration sample even though there are several known

and unknown variables which affect the absorbance in the UV spectrophotometer.

3.4.2.2 Sample Preparation: 0.5 ml of diphenylcarbazide were added to 0.5 ml of sample in a glass bottle. The total volume was filled up to 20 ml with ultrapure water (17 ml).

3.5 Adsorption Isotherms

Adsorption models are needed to characterize the adsorption process under thermodynamically constant conditions. Generally, the amount of material adsorbed is determined as a function of the concentration at a given temperature, and the resulting function is called an adsorption isotherm (Metcalf and Eddy 1985). Various adsorption isotherms such as Langmuir, Freundlich, Redlich-Peterson, Brunauer, Emmet and Teller (BET) have been used to characterize adsorption (Pauline et al., 2001). However Langmuir and Freundlich are commonly used to fit data for biosorption (Feng and Aldrich, 2004)

3.5.1 Langmuir Isotherm

Langmuir isotherm is the most commonly used isotherm. It is defined as

$$q_{eq} = \frac{q_{\max} k C_{eq}}{1 + k C_{eq}} \qquad \text{Eq. No 2}$$

Linearizing:

$$\frac{C_{eq}}{q_{eq}} = \frac{C_{eq}}{q_{\max}} + \frac{1}{q_{\max} k} \qquad \text{Eq. No 3}$$

where

C_{eq} = final equilibrium concentration (mg L^{-1})

q_{eq} = mass of adsorbate adsorbed per unit mass of adsorbent at final equilibrium

concentration (mg g^{-1}). This is also described as the surface coverage.

q_{max} = maximum adsorption capacity (mg g^{-1})

k = Langmuir equilibrium constant, related to the affinity of the binding sites (l mg^{-1})

The Langmuir parameters, q_{max} and k can be found from the slope and intercept of a C_{eq}/q vs. C_{eq} linear plot. Henceforth, q_{max} = $slope^{-1}$ and k = $intercept^{-1}$ x slope. The isotherm has been developed based on the following assumptions (Stumm and Morgan, 1996):

(i) Monolayer coverage on the adsorption surface

(ii) All adsorption sites are energetically equal and henceforth have an equal affinity for adsorbate

(iii) Only one molecule will react with one active site

(iv) No interaction (attraction or repulsion) between molecules on adjacent sites exist.

(v) Equilibrium is reached in the adsorbate- adsorbent system.

The isotherm starts out with a steep initial increase in the amount adsorbed with concentration, followed by a much smaller increase in the amount adsorbed per unit change in concentration. The curve continues to increase, but at higher concentration, the isotherm will approach a limiting value of q_{max} of the adsorbent.

3.5.2 Freundlich Isotherm

The Freundlich relationship is an exponential empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration range [Volesky, 2003b].

$$q = kC_e^{1/n} \qquad \text{Eq. No 4}$$

Linearlizing,

$$\log q = \log k + \frac{1}{n}\log C_e \qquad \text{Eq. No 5}$$

where q represents the amount of metal ions adsorbed at equilibrium (mg g^{-1}), C_e equilibrium concentration (mg L^{-1}), k the measure of adsorption capacity, and $1/n$ is adsorption intensity and includes other parameters. A plot of log (q) versus log C_e gives a straight line, the slope and intercept of which correspond to $1/n$ and log k, respectivelywhere k and n are Freundlich constants. The Freundlich constant 'n' is a measure of non linearity, relating the variability/uniformity of the binding sites, and has the value: 0 <n < 1. If n=1, the equation will result in a linear form. This means that the sites have the same binding strength. On the contrary, if n<1, the average binding energy will decrease with increasing adsorption density and thus resulting in non-linear isotherm [Ruthuven, 1992].

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Biosorption of Chromium (VI) and Chromium (III) by *Sargassum* and *Ulva*

The most important experimental parameters such as initial pH, quantity of adsorbent, initial metal ion concentration, and contact time that infleunce biosorption were investigated and optimized to maximize the removal efficiency of Cr from aqueous solution. The results obtained from this investigation are discussed below.

4.1.1 Effect of pH

The effect of pH on the Cr(VI) adsorption was investigated over a pH range of 1.0 to 8.0 for *Sargassum* and *Ulva*, and the results are shown in Figure 4.1. The maximum uptake of Cr(VI) onto *Sargassum* and *Ulva* was observed at low pH (pH 1 - 2).

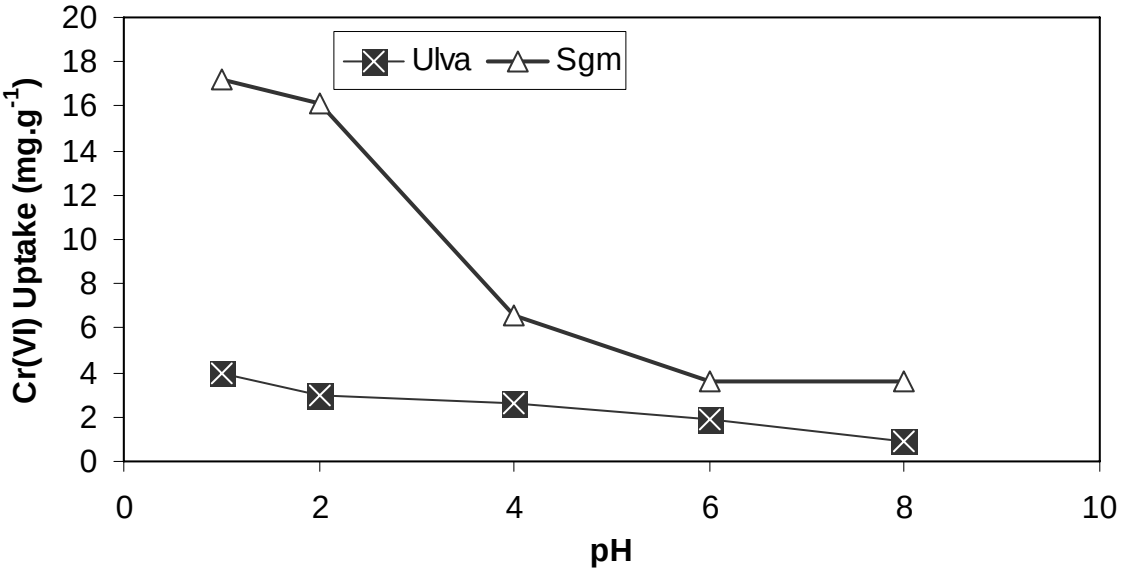

Figure 4.1
Effect of pH on adsorption of Cr (VI) ions by *Sargassum* and *Ulva*

The adsorption percentage decreased with increase in solution pH. As illustrated in Figure 4.1, the Cr uptake rate for *Sargssum* was approximately 17 mg g^{-1} (60% removal) while the same for *Ulva* was relatively lower, only 4 mg g^{-1} with an adsorption efficiency of 17%. As can be seen, the low pH enhances the adsorption of Cr(VI) onto both biosorbents. There is a sharp decrease in the biosorption of Cr(VI) with increase of the solution pH. This is because at low pH the dominant species of Cr ions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, $Cr_4O_{13}^{2-}$ and $Cr_3O_{10}^{2-}$ could be expected to interact more strongly with the positively charged particles on the biosorbents surface. This observation is consistent with previous reports in the literature on the biosorption of Cr(VI) onto *Sargassum* (Kratochvil et al., 1998).

Biosorption of Cr(VI) ions to seaweeds takes place by passive mechanisms. The interaction between metal ions and seaweeds depends not only on the nature of the biosorbents used, but also on the solution chemistry of the metal to be removed. Cr exhibits different types of pH-dependant equilibrium in aqueous solution (Rollinson, 1973), the most important of which are the following:

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \quad - \quad (1)$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \quad - \quad (2)$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2H_2CrO_4 \quad - \quad (3)$$

In acidic solutions, the equilibrium is as follows

$$HCr_2O_7^- \leftrightarrow Cr_2O_7^{2-} + H^+ \quad - \quad (4)$$

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \quad - \quad (5)$$

The equilibrium in alkaline pH is given as follows

$$Cr_2O_7 + OH^- \leftrightarrow HCrO_4^- + CrO_4^{2-} \quad - \quad (6)$$

$$HCrO_4^- + OH^- \leftrightarrow CrO_4^{2-} + H_2O \quad - \quad (7)$$

Above pH 8, CrO_4^{2-} is the only species that can exist in the solution. As the pH is shifted, the equilibrium will also shift. In the pH range 2.0 - 6.0, $HCrO_4^-$ and $Cr_2O_7^-$ ions are in equilibrium. At lower pH (pH < 2) values, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species are formed (Hunt, 1965). Thus a decrease in solution pH could lead to the formation of more polymerized Cr oxide species.

The solution pH also influences the electrostatic binding of metal ions to biosorbent functional groups. The increased binding of Cr(VI) ions, which exist as negatively charged oxo-anion complex at low pH, can be explained as due to electrostatic binding to positively charged groups of the biosorbents. Since the the maxium uptake of Cr(VI) was observed at about pH 2, pH 2 was choosen for further studies in order to minimise the volume of acid needed for adjusting the pH to lower levels.

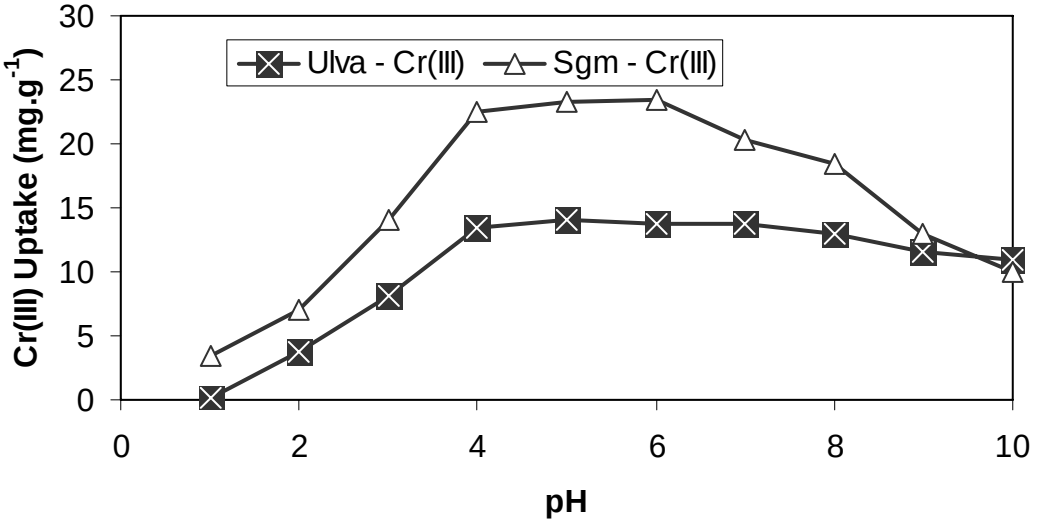

Figure 4.2
Effect of pH on adsorption of Cr (VI) ions by *Sargassum* and *Ulva*

The effect of pH on the removal of Cr(III) was examined for both *Sargassum* and *Ulva*. The results are shown in Figure 4.2. As can be seen from Figure 4.2, the uptake rate of Cr(III) were greater at high pH. Low uptake of Cr(III) by *Sargassum* and *Ulva* at low pH was apparently caused by an increased ability of protons to compete with Cr(III) for the binding sites in the biomasses.

It is well known that cations of Cr(III) dissolved in water undergo hydrolysis and /or complexation reactions, the extent of which depends primarily on the total Cr(III) concentration, pH, and the type of anions present in the solution. The hydrolysis of Cr(III) can be expressed as follows:

$$Cr^{3+} + H_2O \leftrightarrow Cr(OH)^{2+} + H^+ \qquad - \qquad (8)$$

As can be seen, this reaction generates divalent cations $Cr(OH)^{2+}$ and protons which contribute to the increased acidity of Cr(III) solutions. It is the involvement of protons in the reactions which may lead to incorrect interpretations of the pH changes in the system. Cr(III) precipitartion at higher pH in aqueous solution is an irriversible reaction and further adition of ammonium acetate after the precipitation will not help to dissolve the precipitate. Several experiments were repeated, and solutions were prepared again whenever precipitation was observed. Under neutral to basic conditions, Cr (III) tends to precipitate out, while under acid conditions it will tend to solubilize. While chromate and dichromate ions are extremely water soluble at all pHs, they can precipitate with a number of divalent cations.

Cr(III) were precipitated at high pH, even though ammonium acetate was added to control the precipitation. At higher pH level (pH >7) Cr(III) was precipitated in the ionic solution and this

causes the solution to be turbid. There were negligible, or no precipitation occurring at lower pH level and hence a neutral pH level (less than 7.0) was used for further studies. At higher pH level the precipitation of Cr(III) salt became dominant phenomenon, and the adsorption or reduction process may not be the removal mechanism for Cr(III) ions or salts from the aqueous solution.

Apart from the adsorption of Cr(VI) ions, *Ulva* showed adsorption capacity similar to what has been observed with *Sargassum* for Cr(III) ions. Almost 70% of the total Cr present as Cr(III) ions was removed by *Ulva* compared to more than 80% removal by *Sargassum*. Sheng et al., (2004) employed infrared spectroscopy to show the chelating character of the metal ion coordination to the carboxyl group in the brown seaweed. The authors demonstrated that the functional groups involved in bivalent metal sorption included carboxyl, ether, alcoholic and amino groups, but concluded that sulfonate groups were not mainly responsible for metal sorption. The results of some other studies claimed that ion exchange is the main mechanism for the sorption of cationic metal ions onto marine seaweed (Williams and Edyvean, 1997 and Kratochvil et al., 1998). Several studies confirmed that the biosoprtion mechanism by seaweed for Cr is a combination of adsorption and reduction (Kratochvil et al., 1998). By analyzing Figures 4.1 and 4.2 on the removal efficiency of *Sargassum* and *Ulva* for Cr(VI) and Cr(III) ions, it can be concluded that the reducing capability of *Ulva* is much lower compared to that of *Sargassum*.

4.1.2 Effect of varying Biomass Concentration

The optimium biomass quantity for *Sargassum* and *Ulva* was determined by adding 0.05 - 0.25 % (w/v) of the biosorbet into the ionic solution. The optimum quanity of *Sargassum* and

Ulva biomass was observed as 0.1% (w/v). All other experiments were conducted using 0.1% (w/v) of *Ulva* and *Sargassum*.

4.1.3 Effect of initial metal ion concentration

The adsorption percentage determined at different initial Cr(VI) concentrations for each bio-sorbent is illustrated in Figure 4.3**.** For *Sargassum* and *Ulva*, higher percentage removal of both Cr (VI) and Cr(III) ions were observed at lower initial concentrations (< 100 mg L^{-1}). However, the metal uptake capacity i.e. the quantity of metal adsorbed per unit weight of the sorbent displayed a reverse trend and the maximum adsorption capacity for Cr(VI) and Cr(III) by *Sargassum* was at 200 mg L^{-1} and by *Ulva* was observed at 500 mg L^{-1}.

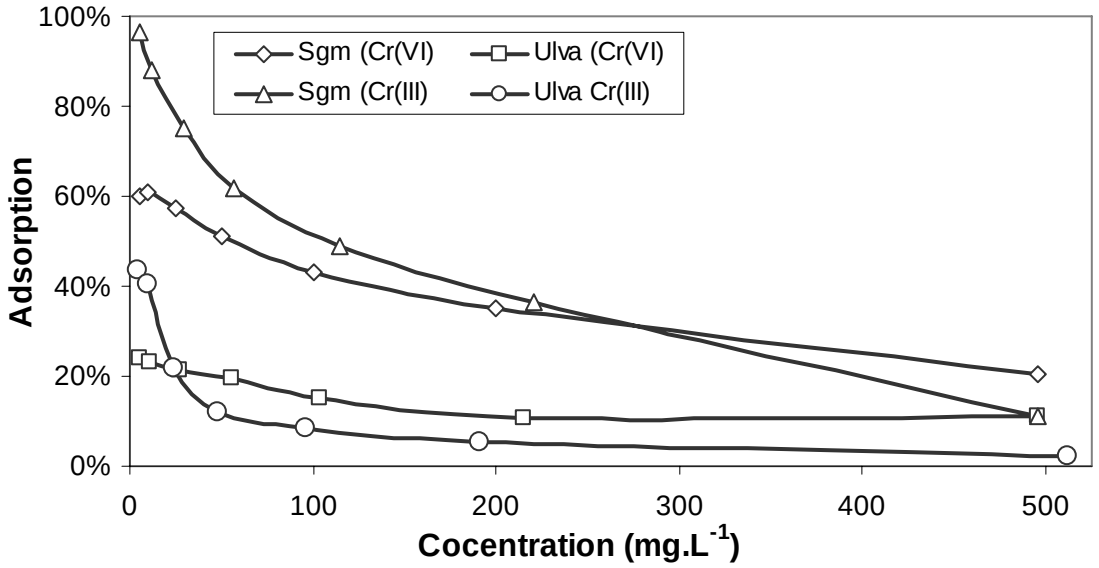

Figure 4.3
Effect of varying initial concentration of Cr(VI) and Cr(III) ions on biosorption by *Sargassum* and *Ulva*.

The rate of adsorption is a function of initial concentration of ions. The reduction in adsorption percentage at higher initial concentration of Cr(VI) ions could be explained as follows. As the

quantity of sorbent is kept uniform, the number of ions competing for the available binding sites on the biomass increases at higher initial concentrations of the sorbate. As a result of this, more ions are left un-adsorbed in solution due to biosorbent saturation and a lack of binding sites for further complexation of Cr ions.

However Cr uptake (mg Cr g^{-1} biomass) increased at higher concentration of Cr ions. This is because of the number of ions adsorbed from solution of higher concentrations is more than that removed from less concentrated solution. Therefore the percentage of ions adsorbed at higher concentration levels showed a decreasing trend whereas the uptake of ions displayed an opposite trend.

4.1.4 Kinetics of Cr(VI) and Cr(III) adsorption

In order to determine the time required for reaching sorption equilibrium, experiments were carried out for six hours and samples analyzed at regular intervals. As illustrated in Figure 4.4,

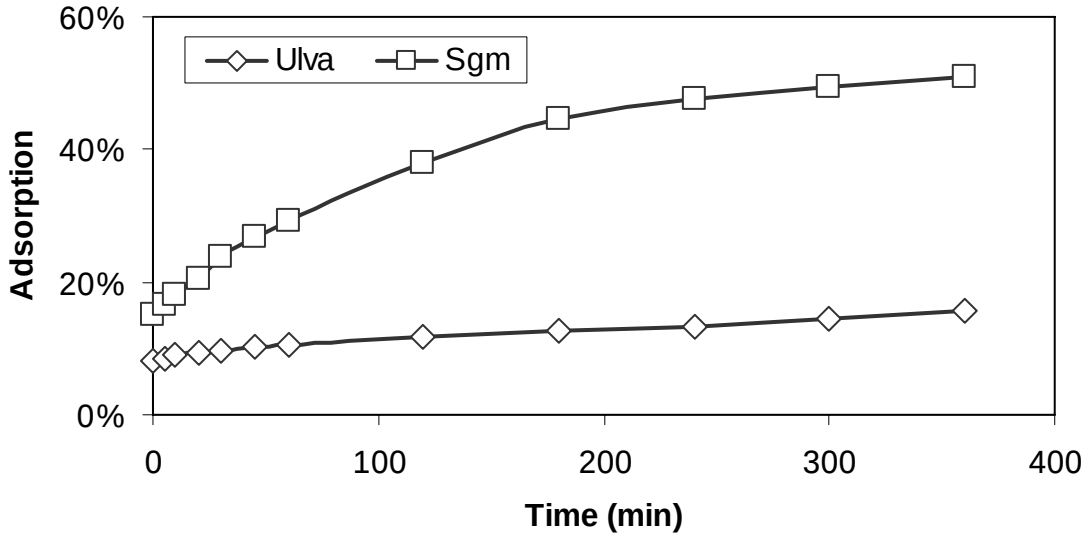

Figure 4.4
Kinetics of Cr (VI) adsorption by *Sargassum* and *Ulva*

Cr(VI) adsorption by *Sargassum* and *Ulva* is a slow process, and the time taken for reaching the equillibrium of adsorption by *Sargassum* was 4 hours. *Ulva* showed slow adsorption efficiency even after 6 hours. The maximum adsorption (percentage) achieved after 6 hours for *Sargassum* was 51%,, which is much higher compared to that of *ulva* (16%). After four hours the rate of adsorption were reduced for *Sargassum* seaweed, this is due to the kinetics of metal adsorption, which depends on physical adsorption onto the cell surface which is usually rapid during the early period of contact between the sorbent and the sorbate.The active adsorption sites of the adsorbent get involved in Cr complexation as soon as the adsorbent is introduced into the system, which shows that prolonged contact between the adsorbent and the adsorbate may not yield better adsorption. The rapid adsorption observed for *Sargassum* in this study is consistent with several earlier reports on biosorption of other metals (Chang et.al., 1997).

As shown in Figure 4.4 the rate of adsorption of Cr(VI) ions by *Ulva* was very low compared to that of *Sargassum,* the adsorption curve is a straight line with a almost zero slope. This shows that the adsorption of Cr(VI) ions by *Ulva* is not only a slow process, but also the saturation of adsorption sites in *Ulva* is not completed even after 6 hours. Another experiment was conducted to verify the adsorption and equillibrium kinetics of *Ulva*, it showed even after 24 hours of continuous agitation the percentage adsorption remained 17%. There are limiting factors that affect the adsorption of Cr (VI) by *ulva* compared to *Sargassum* seaweeds.

Kinetic experiments were conducted using *Sargassum* and *Ulva* for Cr (III), and the results are plotted in Figure 4.5. Both sorbents showed a similar trend for the adsorption for Cr (III) ions compared to Cr (VI) ions. Almost 50% of the metal ions were adsorbed by both biomasses within an hour of exposure and 70% adsorption within 6 hours. In both experiments the total

Cr concentrations were measured by ICP-OES.

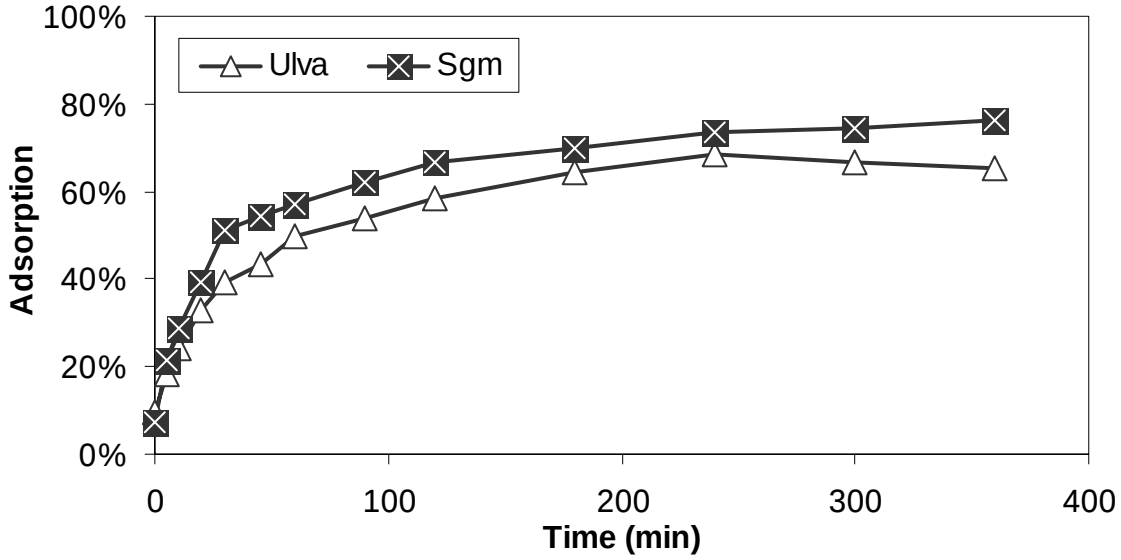

Figure 4.5
Kinetics of Cr(III) adsorption by *Sargassum* and *Ulva*

The rapid adsorption equilibrium for Cr(III) ions by *Sargassum* and *Ulva* is an indication of the availability of adsorption sites on the surface of these biomass was readily available for adsorption. On the other hand, the faster adsorption equilibrium of Cr(III) ions than that of the Cr(IV) ions by both the sorbents suggests that the adsorption rate of Cr on the seaweeds was probably more attachment-controlled than transport-controlled, as both the Cr(III) and Cr(VI) species may essentially have similar transport rates from the bulk solution towards the surfaces of the fibers in the experiments which used the same initial Cr concentrations.

When the attachment of the Cr(III) species on the seaweeds was more favorable than that of the Cr(IV) species, the Cr(III) species transported to the surfaces of the seaweeds can be more instantly adsorbed to the surfaces of the biomass and thus achieve a faster adsorption equilibrium. In order to study the kinetics of Cr(VI) adsorption over time a separate experiment

was conducted upto 24 hours, Cr(III) and Cr(VI) concentrations were measured and the results are plotted in Figure 4.6.

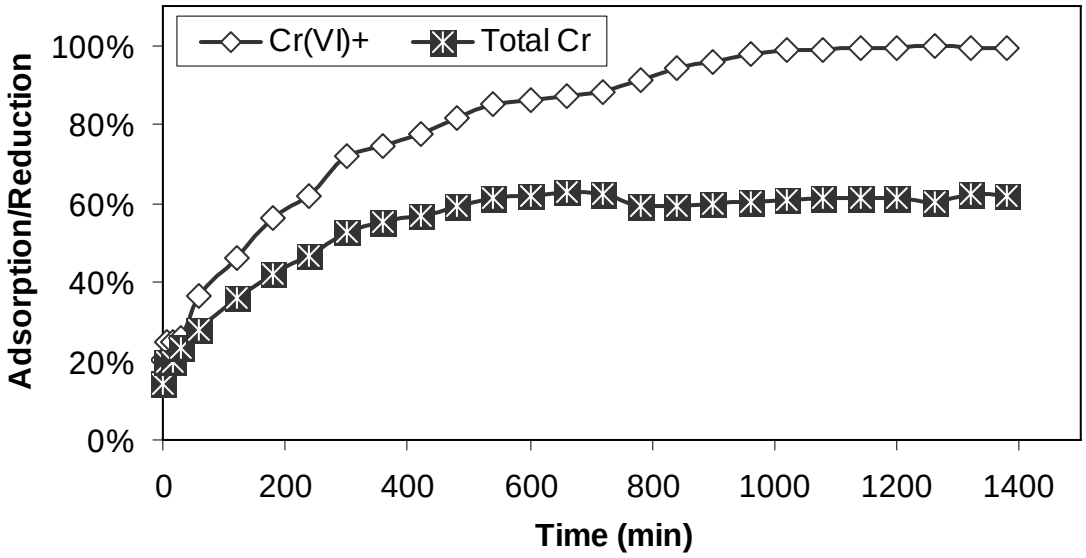

Figure 4.6
Kinetics of Cr(VI) adsorption and reduction by *Sargassum*

As can be seen from this Figure, 20 % of the Cr(VI) ions in the solution was instantaneously reduced and/or adsorbed by *Sargassum* biomass. The kinetic rate of reduction of Cr(VI) ions was well ahead than the kinetic rate of adsorption of total Cr ions in the solution**.** 100% of Cr(VI) ions were reduced within 20 hours of time. Adsorption reached equillibrium after 8 hours and remained at 60%. Park et al., (2004) concluded, after studying the Cr(VI) adsorption and reduction mechanism, that Cr(VI) was removed from aqueous phase through both direct and indirect reduction mechanisms. Generally, the reduction of Cr(VI) to Cr(III) depends on various factors such as the nature of the adsorbent, the concentration of Cr, and the equillibrium time. In some cases, the adsrption is completed through reduction, whereas in other cases, it is partially anionic and partially reduction. Many studies have been reported in

the literature which show that the adsorption of Cr(VI) is completely anionic (Dinesh et al., 2006). Cr(VI) ions in the solution was disappeared due to the reduction reaction in the aqueous phase, the reduced Cr ions were adsorbed into the biomass. There were no further adsorption observed after 10 hours even though more Cr(III) ions were formed in the solution.

A similar experiment was conducted using *Ulva* but the reduction as well as the adsorption process was very slow even after 24 hours of exposure. Comparing the adsorption and reduction experimental results for Cr(VI) and Cr(III) ions by *Sargassum* and *Ulva*, it can be concluded that the rate of reduction and the overall reduction capacity of *Ulva* are much lower compared to those of *Sargassum*.

4.1.5 Adsorption Isotherm for Sargassum and Ulva

The experimentally determined sorption isotherms over a concentration range of 5 - 500 mg L^{-1} of Cr(VI) and Cr(III) ions are presented in Figure 4.7.

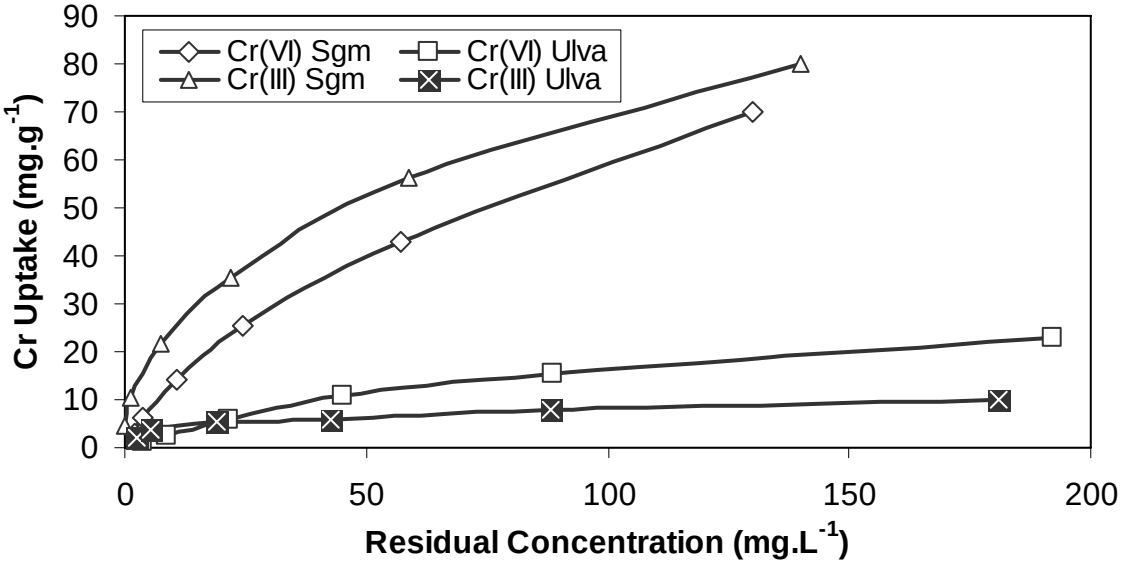

Figure 4.7
Experimental sorption isotherm for adsorption of Cr(VI) and Cr(III) ions from aqueous solution by seaweeds.

The steepness of the isotherm indicated the strength of affinity of the biosorbent for Cr(VI) and Cr(III) ions. As depicted in figure 4.7, the steepness of the isotherms was decreased tremendously for *Ulva* compared to *Sargassum* for two ionic species of Cr, thereby indicating the lower chromium adsorption potential for *Ulva* compared to *Sargassum*.

Among these two seaweeds and different adsorbates (Cr(III) and Cr(VI)) *Sargassum* exhibited the highest adsorption efficiency and could take up approximately 61 mg of Cr(VI) ions and 58 mg of Cr(III) ions per gram of *Sargassum* biomass. The uptake rate for *Ulva b*iomass was 36 and 11 mg of Cr(VI) and Cr(III), respectvely. This is due to the lesser quantity of carboxylic group in *Ulva* biomass compared to the concentration of carboxylic group in *Sargassum* biomass. Virtually no covalent metal binding occurred in *Ulva* possibly because green algae, which lacks the presence of alginate, do not offer carboxyl groups spaced at a suitable distance for bridging of one metal ion between two binding sites.

The number of weakly acidic carboxyl groups was determined by Schiewer and Volesky (2000). They reported, 2.9 for *Petalonia*, 2.6 for *Sargassum*, 1.5 for *Colpomenia,* and 1.1 for *Ulva*. The study of biosorption in Cu by Schiewer and Volesky (2000) also reported that the Cu binding constants decreased in the order *Sargassum* > Petalonia > Colpomenia > *Ulva* ≈ 0. These results indicated that brown algae are more suited for biosorption applications than *Ulva* because of their high metal binding capacity and affinity. *Sargassum* excels in also being more stable (less swelling and leaching) and is therefore the most promising biosorbent than *Ulva* biomass.

The studies by the same group (Schiewer and Volesky 2000) also reported that the determined

number of binding sites decreased in the order Petalonia ≥ *Sargassum* > Colpomenia > *Ulva*. Due to thethe high number of avaiable binding sites, *Sargassum* and Petalonia are most promising for biosorption applications (Schiewer and Volesky (2000). This explains the reasons for lower adsoprtion capability of *Ulva* compared to *Sargassum* biomass.

4.2 Adsorption of Cr(VI) by pre-treated Biomass

Pre-treatment of *Sargassum* and *Ulva* by an alkali (NaOH), acid (HCl), formaldehyde, and acetone was studied. Several experiments were conducted to observe the effect and changes in the adsorption parameters of *Ulva* and *Sargassum* by different pre-treatment processes. As depicted in the Figure 4.8, the pre-treatment with 0.1 N HCl and acetone does not effect the adsorption efficiency of *Ulva* and *Sargassum*, while the treatment with NaOH and formaldehyde reduced the adsorption efficiency of *Sargassum*.

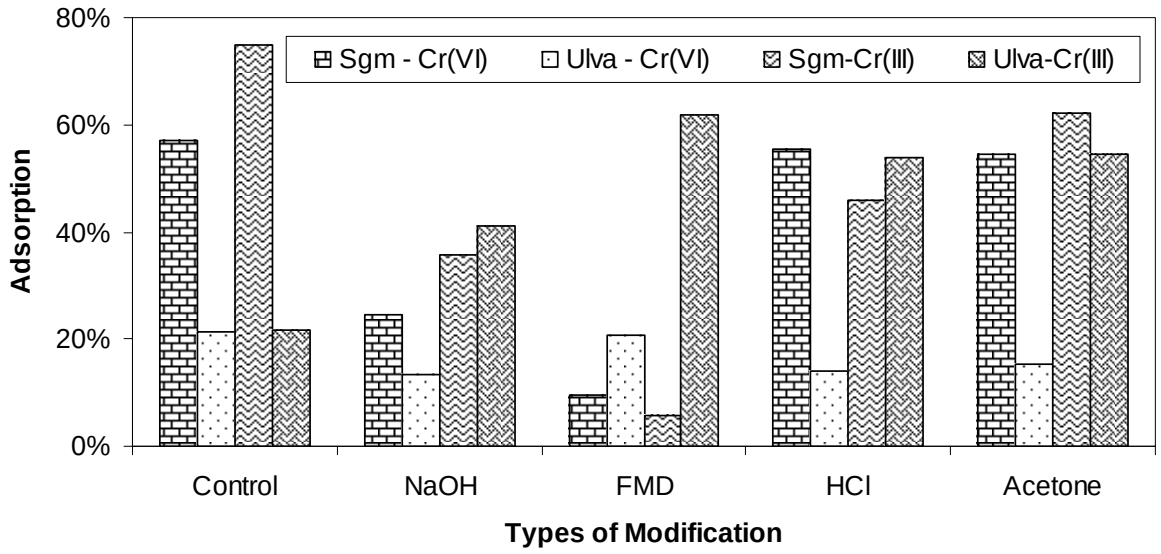

Figure 4.8
Percentage Adsportion of Cr(VI) and Cr(III) ions by chemically modified biomass of *Sargassum* and *Ulva*.

No enhancement or reduction in the adsorption efficiency was observed for *Ulva* biomass. The extraction of finely powdered biomass in acids could expose more binding sites and therefore the accessibility of the sorbate ions to the sorption sites should be increased. Treatment of the biomass with sodium hydroxide resulted in swelling and disintegration of the biosorbent. The adsorption capacity of the alkali extracted biomass was also unfavourably affected and exhibited approximately 25% reduction in percentage removal of Cr(VI) ions by *Sargassum*. Alkali treatments cause hydrolysis of protein constituents, and it also brings about drastic effects such as swelling of biomass, probably due to polymer chain breakage, and thereby hindered the operational stability. Adsoprtion results (Figure 4.8) indicated a decline in Cr binding by the formaldehyde treated *sargassum* biomass. Formaldehyde causes cross linking of adjacent hydroxyl groups in cell wall. The adsorption efficiency of Cr(III) by *Ulva* biomass was substantially increased by the pre-treatment with all chemicals including sodium hydroxide. Formaldehyde shows the highest effect in increase in the adsorption efficiency.

Overall the adsorption efficiency for Cr(III) ions was observed more than that of Cr(VI) ions by *Sargassum* biomass (70% adsorption efficiency compared to 55% for Cr(VI) ions). The various chemical treatment for *Ulva* significantly increased the adsorption efficiency for Cr(III) ions (~60% for Formaldehyde, hydrochloric acid, and acetone pre-treated *Ulva* compared to 20% efficiency for the control samples (without any treatment). The difference in the Cr(VI) and Cr(III) adsorption efficiency by both biomass can be explained by the availability of the adsorption sites for the adsorbent ions.

The maximum uptake rate for different biomass for different metal ions was plotted in Figure 4.9. Formaldehyde, hydrochloric acid, and acetone pre-treatment enhnaced the adsorption

capacity of *Sargassum* for Cr(VI) ions. All the chemical pre-treatments reduce the uptake rate of *Sargassum* for the adsorption of Cr(III) ions. The uptake of Cr(VI) and Cr(III) ions was increased by pre-treatment of *Ulva* with acetone, all other pre-treatments do not show any effect in the uptake rate for *Ulva* biomass.

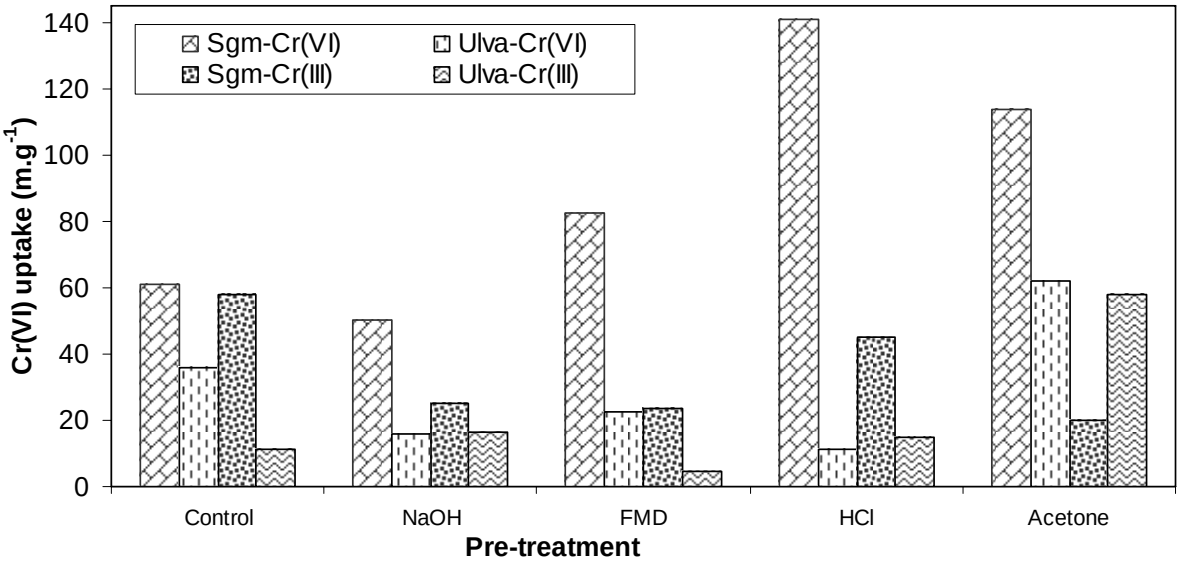

Figure 4.9
Adsportion uptake of Cr(VI) and Cr(III) ions by chemically modified biomass of *Sargassum* and *Ulva*.

The mass balance for protons is

$$q_{H,i}m + [H]_{add}V_{Hiadd} - [OH]_{add}V_{OH,add} + [H]_i V_i = q_H m + [H]V(mM) \qquad (9)$$

where [H] is the concentration of protons in solution, q_H is the amount of protons bound to the biomass, m is the mass of biosorbent, and V is the solution volume. The subscript i denotes initial values, otherwise final values are referred to. $[H]_{add}$ and $[OH]_{add}$ are the concentrations of added acid or base, respectively, with their solution volumes being $V_{H,add}$ and $V_{OH,add.}$

The mass balance for a divalent metal ion M is

$$0.5q_{M,i}m + [M]_i V_i = 0.5q_M m + [M]V(mM) \qquad (10)$$

whereby q_M is the amount of metal bound to the biomass (mequiv/g) and [M] is the metal concentration in solution. The factor 0.5 is required to convert from equivalent to molar concentration

For *Ulva*, the exchange constants for any stoichiometry are 1 order of magnitude lower than for the other algae (Schiewer and Wong 1999). That means both ions of Cr can displace protons more easily from the other biosorbents than from *Ulva*. *Ulva* is therefore less suitable for both ions of Cr biosorption because it shows comparatively less affinity for metal ions.

Carboxyl groups are probably the main binding site in both seaweeds since the number of weakly acidic carboxyl groups determined in pH titrations (Schiewer and Wong, 2000) corresponds well to the metal binding capacity B_t. One might therefore at first suspect that these should display the same metal binding constants. However, there is a marked difference in the molecular environment of the carboxyl groups in green and brown algae, respectively. In brown algae, carboxyl groups occur mainly in alginate, a polysaccharide composed of mannuronic and guluronic acids. Green algae, on the other hand, do not contain alginate (Schiewer and Wong, 2000). Their carboxyl groups will therefore rather be present in either protein or complex hetero-polysaccharides of the cell wall containing some uronic acids. Since divalent metals often need two binding sites at suitable distance in order to form a stable complex, the lesser affinity in *Ulva* may be caused by a lack of a suitably spaced sites, i.e., the individual carboxyl sites may be too far apart to allow bidentate binding.

Schiewer and Wong (2000) reported the effect of pH by the addition of various seaweeds in de-ionized water. When 0.1 g of the protonated biomass was equilibrated in 40 ml of deionized water, the final pH ranged between 5.1 (for Petalonia) and 3.0 (for *Ulva*). The release of protons responsible for this drop of pH may due to the presence of excess acid, which had not been removed by washing with de-ionized water after treatment with mineral acid. It cannot be caused by a release of protons from dissociated acidic groups because no other cations were present to balance the negative charge of dissociated acidic groups. Therefore, even if protons were dissociated from the acidic sites, they would be retained in the biomass by electrostatic attraction to the negatively charged groups. From the pH drop in de-ionized water the quantities of excess acid in different biomasses were calculated (Schiewer and Wong, 2000) as 0.025, 0.016, 0.0032 and 0.40 $mmol.g^{-1}$ for *Sargassum*, *Colpomenia*, *Petalonia* and *Ulva*, respectively. This quantity of excess acids in *Ulva* biomass was significantly a high number compared to that of other brown seaweeds including *Sargassum*. The concentration of excess proton in *Ulva* is much higher when compared to the available adsorption sites in *Sargassum* since *Sargassum* has higher number of adsorption sites compared to *Ulva*.

4.2.1 Isotherm Analysis

The two widely accepted and easily linearized equilibrium adsorption isotherm models for single solute systems used in the literature are Langmuir and Frendlich isotherms. The experimental sorption isotherms of the native and modified biomass are depicted in Figs. (4.10 – 4.13). The steepness of the isotherms, which indicated the affinity of Cr(VI) and Cr(III) ions to the biosorbent, decreased in the order HCl-treated > Acetone-treated > Formaldehyde treated > Alkali treated biosorbent. The Cr(VI) uptake for the raw biomass was higher than that

of other chemical pre-treated biomass.

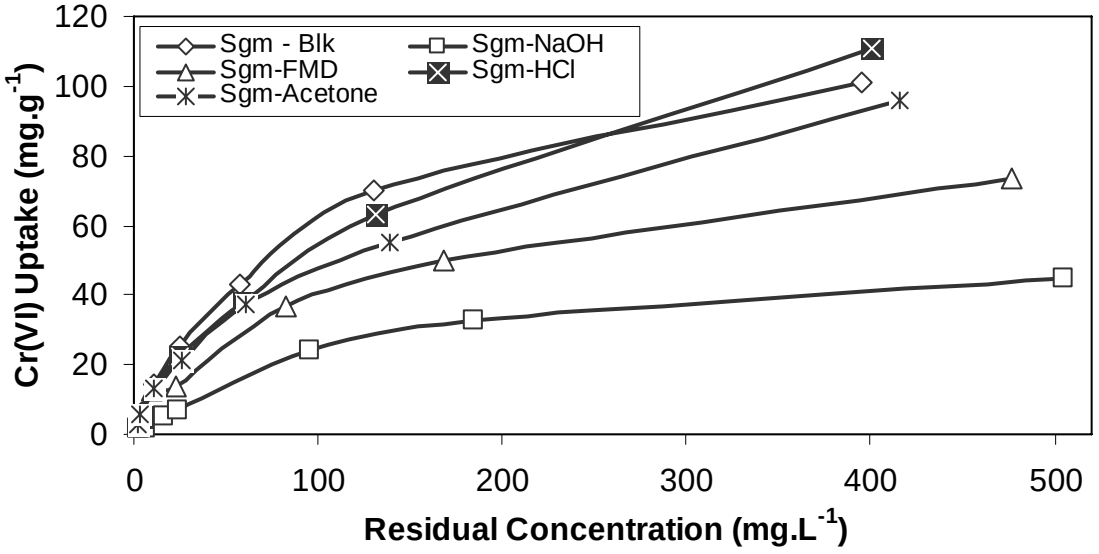

Figure 4.10
Experimental isotherm for Cr(VI) sorption by the unmodified and pre-treated biomass of *Sargassum*

The Cr(VI) adsorption uptake was much higher for *Sargassum* compared to that of *Ulva* biomass, this was explained earlier due to the high number of available adsorption sites in *Sargassum* compared to that of *Ulva*. The pre-treatment by the same chemicals in *Ulva* biomass shows almost the same trend as in *Sargassum* biomass. There was a significant change in the slope of different pre-treaded *Ulva* uptake rates above 200 ppm Cr(VI) concentration. This shows that *Ulva* has a higher Cr uptake capacity at higher metal ions concentrations. At higher concentrations, both biomass shows a lower Cr(III) uptake rate compared to the uptake of Cr(VI) ions. *Sargassum* showed enhanced adsorption uptake by pre-treatment with sodium hydroxide at a residual concentration lower than 100 ppm. Similar uptake rate and trend were shown by the different pre-treated biomass for Cr(IV) and Cr(III) ions. Acetone pre-treated Ulva biomass showed a higher uptake rate for Cr(III) ions.

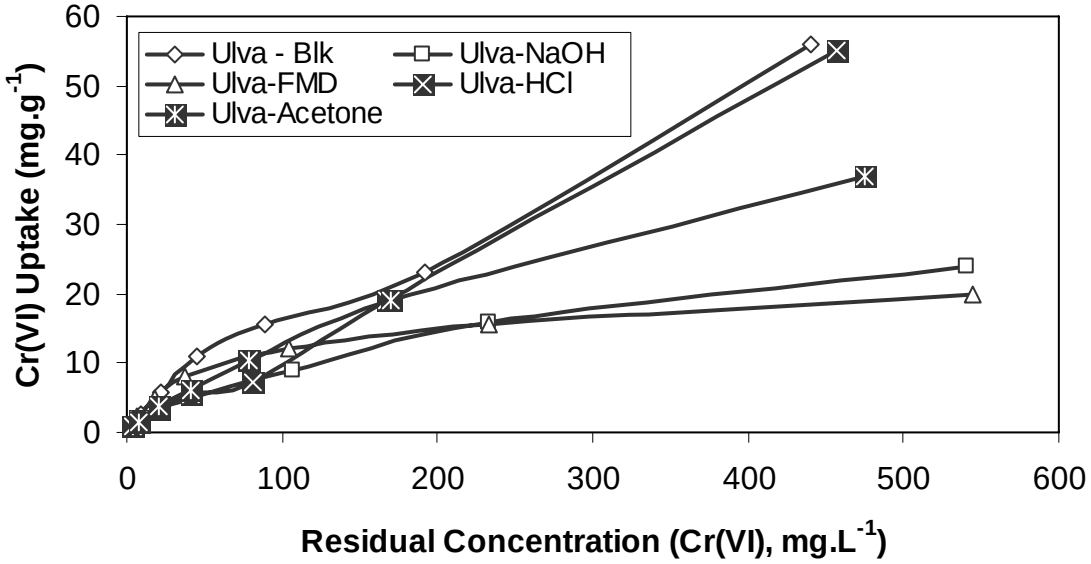

Figure 4.11
Experimental isotherm for Cr(VI) sorption by the unmodified and pre-treated biomass of *Ulva*

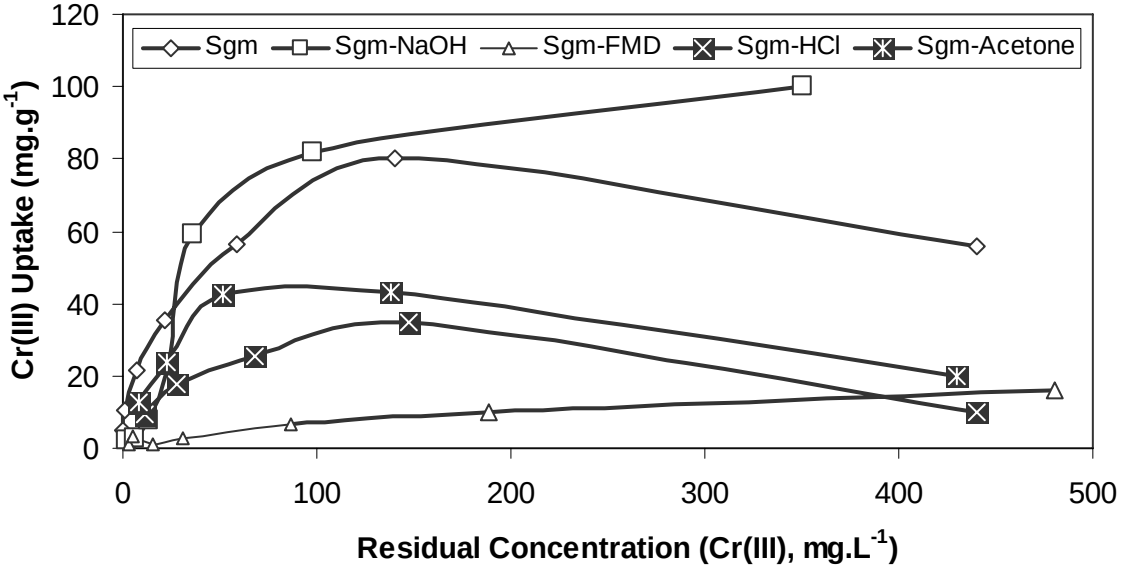

Figure 4.12
Experimental isotherm for Cr(III) sorption by the unmodified and pre-treated biomass of *Sargassum*

The pre-treatment using acetone shows a much higher effect in the Cr(III) uptake rate in the *Ulva* biomass. From the Figure 4.12, it was noticed that the pre-treatment in *Ulva* biomass favorably affects the Cr(III) uptake rates at lower residual concentrations of Cr(III) ions. The adsorption iostherms of pre-treated biomass for Cr(III) removal were plotted on Figure 4.13. At low concentrations, modified *Ulva* biomass shows higher uptake rate. Acetone treated *Ulva* biomass showed higher uptake rate upto a metal ion concentration of more than 100 mg L^{-1}.

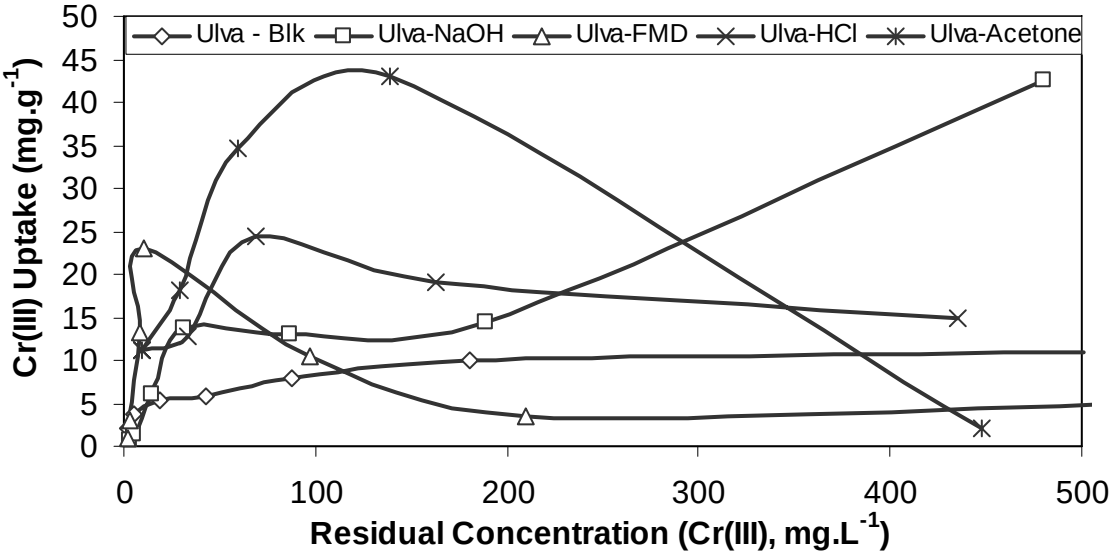

Figure 4.13
Experimental isotherm for Cr(III) sorption by the unmodified and pre-treated biomass of Ulva

The different adsorption parameters for the raw as well as pre-treated biomass are tabulated in Table 4.1. Most of the cases the K_L values are in between 0 and 1 thus the adsorption mechanism is favourable.

The basic evaluation of sorption systems relies on the classical sorption isotherm derived from equilibrium batch contact experiments carried out under controlled environmental conditions.

A quantitative comparison of two different sorption systems can only be done at the same equilibrium (final, residual) concentration. Any other comparison carries an inherent error and can only serve as a qualitative comparison, often used for quick screening purposes. For example, an often-used criterion, the percent of metal removed, does not indicate the concentration range. Even if all experimental parameters are given, this criterion can only result in a qualitative, and relative comparison (better or worse performance) that is adequate only for material screening purposes. The presence of other ions in solution can complicate the evaluation of the sorption system to a large degree, depending on the way the new solute species interact with the sorbent and with the original one.

Table 4.1 Adsorption parameters of pre-treated biomass for Cr(VI) and Cr(III)

	Freundlich Isotherm constants			**Langmuir Isotherms Constants**		
	K_F	N	R^2	Q_0 (mg/g^{-1})	K_L	R^2
	Cr(VI) - Sargassum					
Control	2.11	1.34	0.90	60.98	0.04	0.98
NaOH	1.08	1.93	0.48	50.25	0.01	0.98
FMD	2.46	1.72	0.97	82.64	0.01	0.97
HCl	1.39	1.49	0.99	140.85	0.01	0.96
Acetone	0.56	0.63	0.98	113.64	0.01	0.96
	Cr(VI) - Ulva					
Control	0.34	1.16	1.00	36.10	0.01	0.97
NaOH	0.16	1.07	0.95	15.97	0.01	0.99
FMD	0.66	1.69	0.92	22.42	0.01	0.99
HCl	0.57	1.21	0.98	11.48	0.02	1.00
Acetone	0.60	1.27	0.99	62.11	0.00	0.96
	Cr(III) - Sargassum					
Control	9.01	2.25	1.00	57.80	0.69	0.99
NaOH	0.62	0.92	0.75	25.00	0.38	0.95
FMD	0.61	1.98	0.75	23.64	0.00	0.99
HCl	1.06	1.34	0.98	44.84	0.02	0.99
Acetone	3.21	7.08	0.18	19.76	0.12	0.97
	Cr(III) - Ulva					
Control	2.90	1.15	1.00	11.45	0.04	1.00
NaOH	0.67	1.49	0.81	16.39	0.04	0.96
FMD	3.18	7.29	0.08	4.82	0.69	0.96
HCl	2.74	9.48	0.24	14.97	-0.09	0.99
Acetone	0.44	0.57	0.94	58.14	0.02	0.96

Knowledge of these aspects may not be readily available. Appropriate and meaningful evaluation of a sorbent system with three or more metallic ions becomes very complicated (Volesky, 1995). Evaluation of equilibrium sorption performance needs to be supplemented by process oriented studies of its kinetics and eventually by dynamic continuous-flow tests. The rate of the sorption metal uptake, together with the hydrodynamic parameters, determines the size of the contact equipment. Reaction engineering (Levenspiel, 1999) concepts can be applied to the experimental approach, leading to expression of the values of key process parameters used for comparative, process design, and scale-up purposes. K_F and n are the Freundlich constants characteristics of the system. These parameters denote the adsorption capacity and adsorption intensity, respectively. The value of K_F indicates the sorption capacity of the sorbent, and the higher K_F value indicates the better performance of a sorbent for the particular system. The K_F value for formaldehyde pre-treated *Sargassum* and *Ulva* biomass showed an increase in the adsorption of Cr (VI) ions. Pre-treatment with formaldehyde, hydrochloric acid, and acetone showed an increase in the adsorption capacity of *Ulva* biomass.

Both Langmuir and Frendlich models, which are capable of describing many biosorption isotherms, can hardly have a meaningful physical interpretation in biosorption (Holan and Volesky, 1995). The results cannot be extrapolated, and no predictive conclusions can be drawn for systems operating under different conditions. These simple basic models also do not incorporate the effects of any external variable environmental factors. Moreover, biosorption isotherms may exhibit an irregular pattern due to the complex nature of both the sorbent material and its varied multiple active sites, as well as the complex solution chemistry of some metallic compounds (Holan and Volesky 1995). This phenomenon however, has rarely been recognized, and researchers smooth (bio)sorption isotherm curves by forcing them through

scattered experimental points, or use the preceding simplistic sorption models to fit those data points (Holan and Volesky, 1995).

4.3 REDUCTION OF Cr(VI) TO LESS TOXIC Cr(III)

Hexavalent Cr is a strong oxidizing agent, and it will be reduced to trivalent form in presence of organic matters. Earlier experiments proved that *Sargassum* biomass completely reduces Cr(VI) to Cr(III) within 10 hours of time.

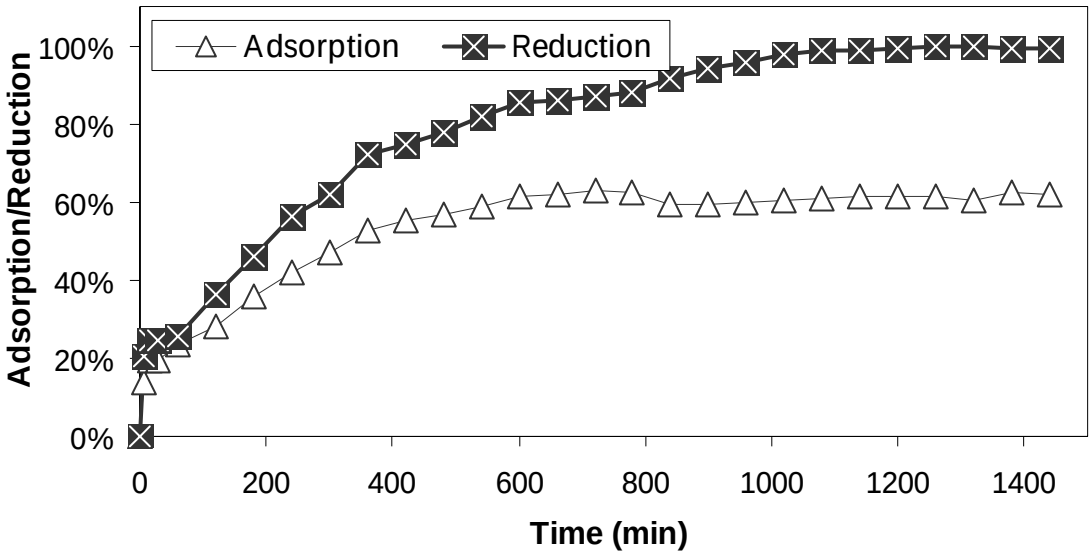

Figure 4.14
Adsorption and Reduction of Cr(VI) ions by *Sargassum*

The removal of hexavalent Cr from aqueous solutions is a coupled process of adsorption and reduction with different kinetic rates. From Figure 4.14 it can be seen that the rate of reduction is much faster than the rate of adsorption of Cr(VI) ions by *Sargassum*. The adsorption of Cr(VI) was affected by the reduction of Cr(VI) to Cr(III) since the anionic adsorption dominates at low pH.

The changes in the Cr(VI) and Cr(III) concentrations in presence of *Sargassum* at different intervals are plotted in Figure 4.15. The initial solution was prepared using potassium dichromate salt and thus only contains Cr(VI) ions. 5 mg L^{-1} of Cr(III) ions was observed in the first sample, that was taken just after the addition of the *Sargassum* biomass (0^{th} minutes) to the solution. The Cr(VI) concentration was reduced to zero mg L^{-1} within 10 hours in the presence of *Sargassum* biomass and the concentration of Cr(III) increased up to 10 mg L^{-1} and adsorption reached equilibrium at 900 mins.

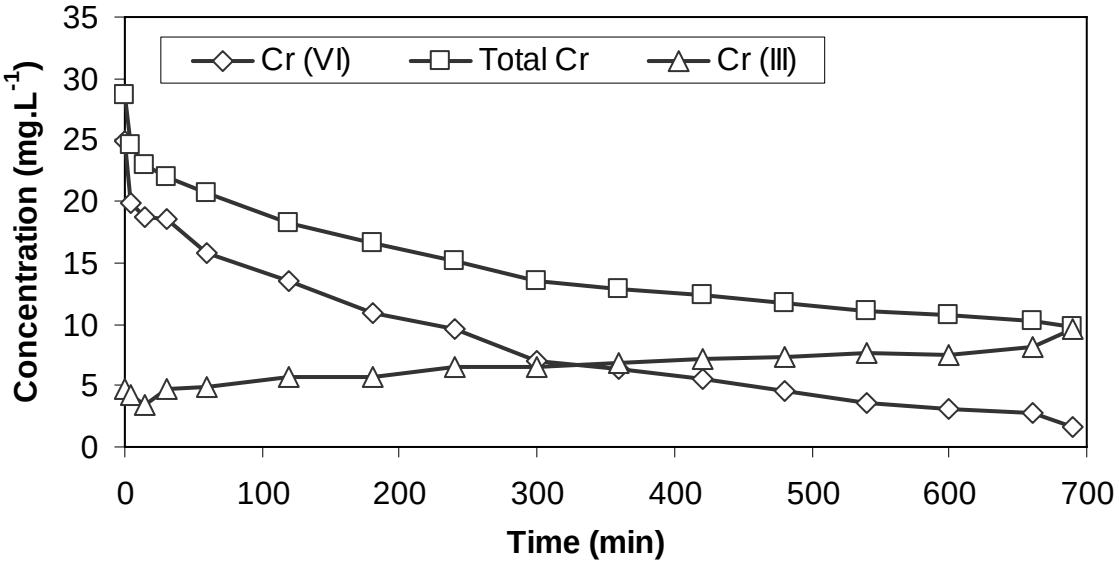

Figure 4.15
Total Cr, Cr(III) and Cr(VI) concentration Vs Time
Adsorption/Reduction by *Sargassum*

The equilibrium concentration of 10 mg L^{-1} is in line with the equilibrium adsorption concentration (60 % adsorption efficiency) found in the adsorption experiments explained in the earlier sections. This proves that *Sargassum* biomass was able to convert 100% of Cr(VI) ions to Cr(III) ions and adsorbed 60% of total Cr ions present in the solution.

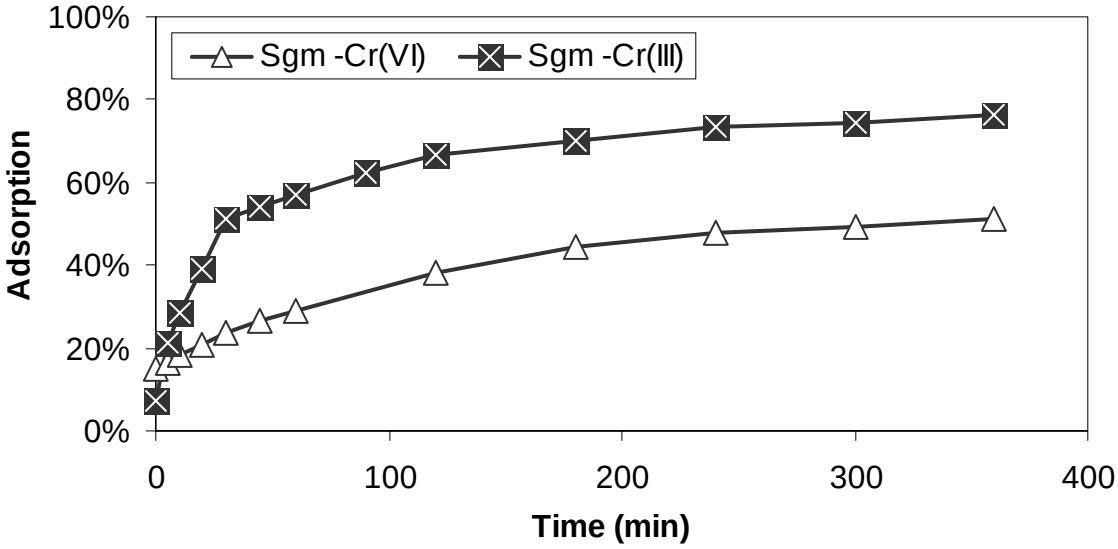

Figure 4.16
Kinetic study for the adsorption of Cr(III) and Cr(VI) ions using *Sargassum*

A comparative experiment for the adsorption of Cr(VI) and Cr(III) ions was conducted, and the results are plotted in Figure 4.16. *Sargassum* showed more affinity for Cr(III) than Cr(VI) and *Sargassum* adsorbed almost 80% of the Cr(III) ions from the solution.

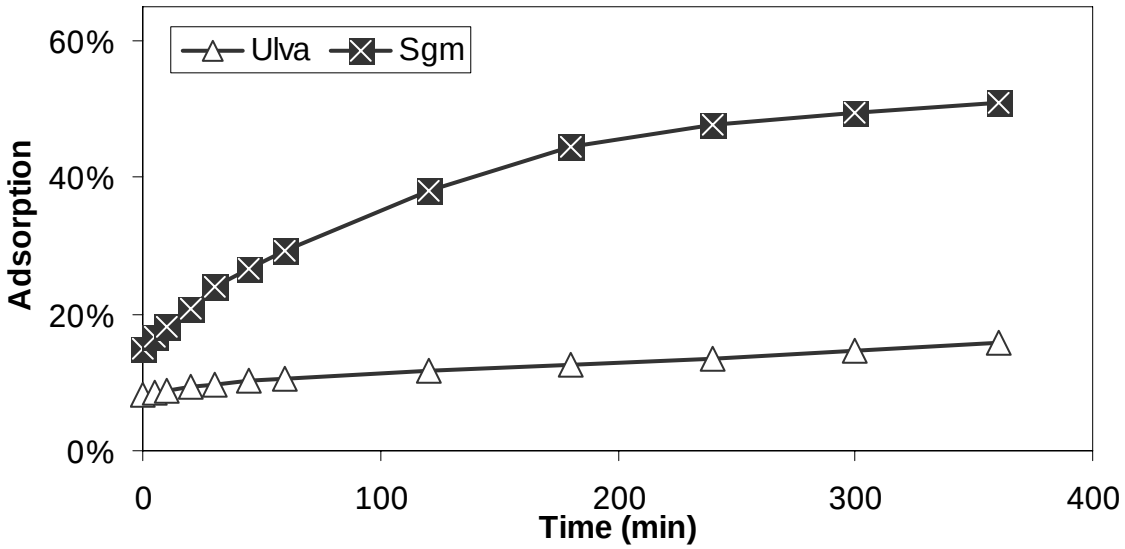

Figure 4.17
Kinetic study for the adsorption of Cr(IV) ions by *Sargassum* and *Ulva*

The kinetic adsorption capacity of *Ulva* was compared with *Sargassum,* and the results are plotted in Figure 4.17. *Ulva* showed lower adsorption capacity to Cr(VI) compared to Cr(III), the details of this analysis and reasons were explained in earlier section for the adsorption of Cr(VI) by seaweeds. Only less than 20% of the Cr(VI) were adsorbed by *Ulva* biomass.

A comparative experiment for the adsorption of Cr(VI) and Cr(III) by using *Ulva* was conducted and the results are shown in Figure 4.18. *Ulva* showed the same level of adsorption as *Sargassum* for Cr(III) ions. Almost 80% of the Cr(III) ions were adsorbed by *Ulva* while only less than 20% of Cr(VI) were adsorbed.

The comparative plots for the adsorption of Cr(VI) and Cr(III) by *Ulva* biomass are shown in Figure 4.18. *Ulva* showed the same level of adsorption as *Sargassum* for Cr(III) ions. Almost 80% of the Cr(III) ions were adsorbed by *Ulva* while only less than 20% of Cr(VI) were adsorbed.

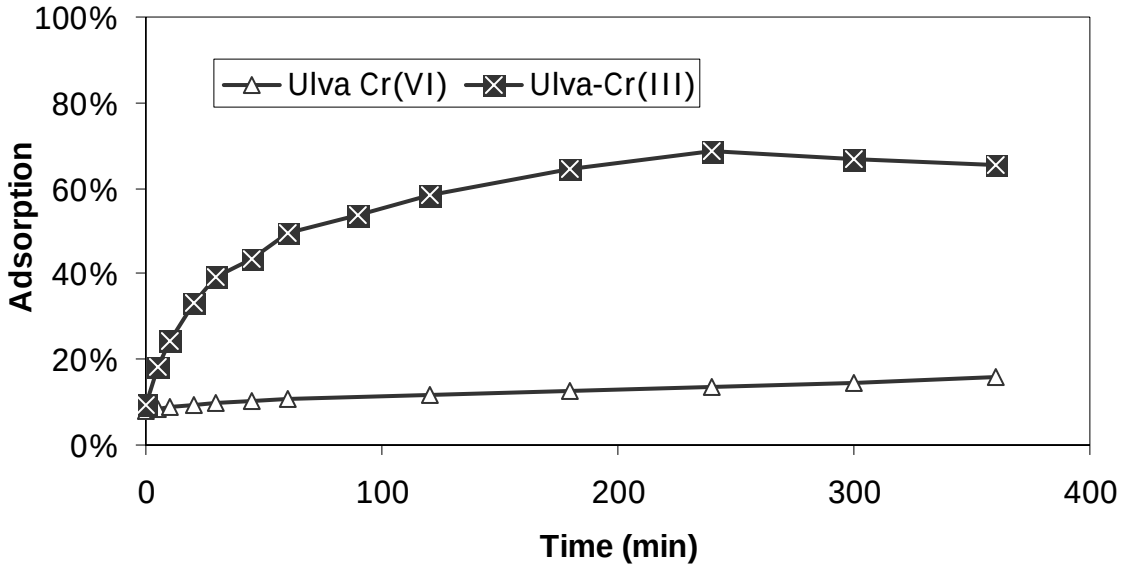

Figure 4.18
Kinetic study for the adsorption of Cr(IV) ions by *Sargassum* and *Ulva*

The results of the adsorption efficiency for *Sargassum* and *Ulva* for Cr(III) ions are plotted in Figure 4.19, and this shows that both seaweeds have similar capability for Cr(III) ions. Adsorption efficiency for *Sargassum* and *Ulva* for Cr(III) ions are plotted in Figure 4.19, this shows that both seaweeds has the similar capability for removing Cr(III) ions from aqueous solutions.

Several researchers reported different novel anionic absorbents as an alternative technology for eliminating Cr(VI) from wastewaters by analyzing only the concentration of Cr(VI) in aqueous solution by a colorimetric method using 1,5-dephenylcarbazide (Park et al., 2006c). Based upon the disappearance of Cr(VI), most of them concluded that the Cr was removed from aqueous solution through anionic adsorption.

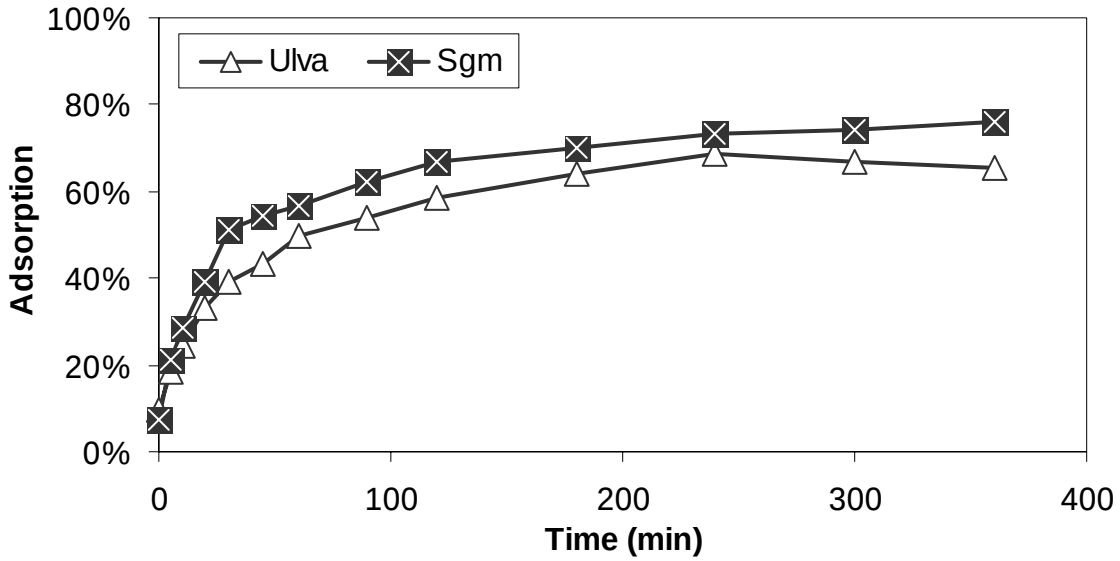

Figure 4.19
Kinetic study for the adsorption of Cr(III) ions by *Sargassum* and *Ulva*

Cr(VI), when in contact with biomaterials at low pH, will easily be reduced to the Cr(III) ions, because Cr(VI) has high redox potential value (above +1.3 V at standard condition) (Gardea et

al., 2000; Deppa et al., 2006). Therefore it is very important to check the reduction of Cr(VI) by tested biomaterials. Cr(VI) adsorption was affected by the reducing effect of seaweed as described earlier. This leads to an interesting findings that both biomass showed similar and high removal rate for Cr(III) ions but very different adsorption behaviour in case of Cr(VI) ions by *Sargassum* and *Ulva* biomass. The removal of Cr(VI) can be enhanced by the reduction of Cr(VI) to Cr(III). Both the seaweeds used in this study have shown much higher adsorption efficiency for Cr(III) ions, and several researchers noted that the removal process of hexavalent Cr is a coupled porcess of adsorption and reduction with different kinetics.

Several experiments were conducted to increase the adsorption efficiency of seaweeds, especially low efficient *Ulva* by using external reducing agent. The experimental data obtained in this study proved that the Cr(VI) adsorption mechanism includes the reduction of Cr(VI) to Cr(III)), and the adsorption efficiency of biomass (*Sargassum* and *Ulva*) has shown a high adsorption efficiency for Cr(III) ions compared to Cr(VI) ions. As part of this study, experiments were conducted to use an external reducing agent to reduce Cr(VI) to Cr(III) and use *Sargassum* or *Ulva* for adsorbing the reduced Cr(III) ions. This will not only help to complete the removal of much toxic Cr(VI) ions, but also enhance the adsorption efficiency of the seaweeds, especially *Ulva* which has a very low comparative adsorption efficiency for Cr(VI) ions with *Sargassum* but a similar adsorption efficiency for removing Cr(III) ions.

Different known chemical reducing agents such as Ferrous ammonium sulfate (FAS), Hydroxylamine hydrochloride, and Ascorbic acids were prepared and used for reducing Cr(VI) ions. The concentration of the chemicals and preparations were described in the materials and method section. Different quantities of these three chemical solutions were added to 25 mg L^{-1}

of Cr(VI) ion solution, and the Cr(VI) ion concentration was measured using a UV spectrophotometer (EPA 7196). Among all the selected chemicals, ascorbic acid showed better reducing capacity and the quantity of ascorbic acid was optimized by adding differnert volume of 1% ascorbic acid solution to the sample. 2.93 moles of ascorbic Acid were required per mol of Cr(VI) for the complete reduction of Cr(VI) ions to Cr(III) ions. Dilute sulphuric acid were used to acidify the samples before adding the reagents for color formation.

Ascorbic acid (chemical name of Vitamin C) is an expensive commercially available reducing agent. The use of such expensive chemical reducing agents makes the biosorption process expensive even though it helps to make use of naturally abundant *Ulva* seaweeds for the effective adsorption of Cr(VI) (reduction of Cr(VI) to Cr(III) by the chemical reducing agent and adsorption of Cr(III) by *Ulva* biomass). This concern led to the investigation of finding another low cost naturally available reducing agent for the effective use with *Sargassum* and *Ulva*.

Several researchers used different organic materials for the removal of Cr(VI) by adsorption as well as reduction process. Several naturally available organic materials such as tea dust, coffee dust, soya bean, soya chunk powder, soya sauce and coir fiber were used to study the reduction capability in order to find a suitable low-cost biomaterial for the effective reduction of Cr(VI) to Cr(III) ions. Used Tea and Coffee dusts were observed to be the most efficient reducing agent, and these powders reduced more than 90% Cr(VI) ions within an hour time (Figure 4.20). The kinetic study for the reduction of Cr(VI) was conducted using tea and coffee dusts, and the results are plotted in Figure 4.20.

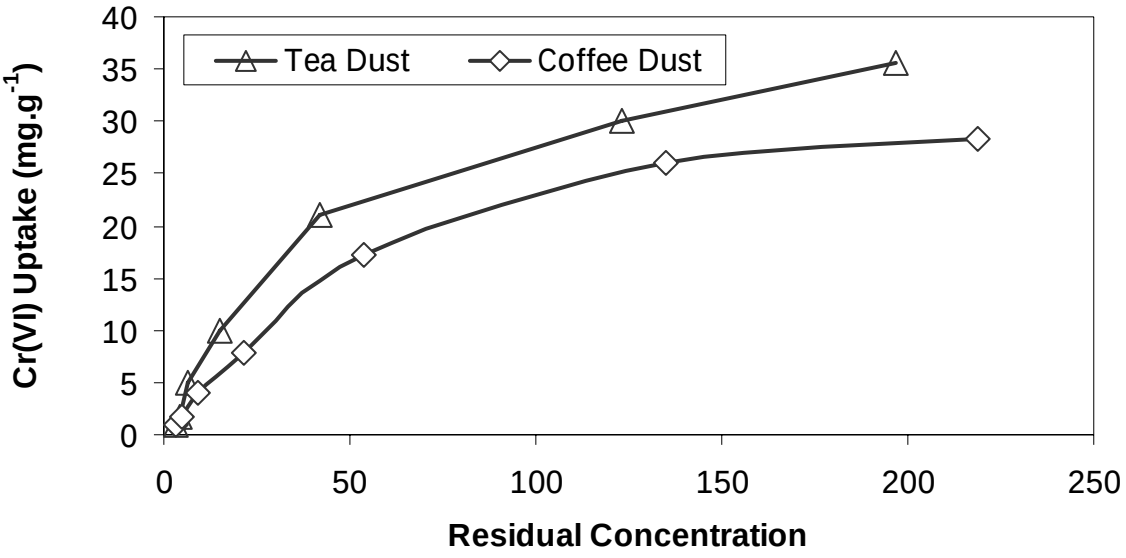

Figure 4.20
Kinetics of the reduction of Cr(VI) ions by Tea and Coffee Dust

Both these materials are capable of reducing more than 80% of Cr(VI) to Cr(III) ions within 1 hour time, and both reduced 100% of Cr(VI) to lower oxidation state within 6 hours of time. Coffee dust instantaneously reduced Cr(VI) to its lower states, the 0^{th} minutes sample (just after the addition of coffee dust to the solution) showed almost 50% reduction.Tea and Coffee dusts were selelcted as potential low-cost biomaterials, and further studies were conducted to optimize the parameters for reduction and adsorption of Cr(VI) from aqueous solutions, The details are described in the next section.

4.4 Use of Coffee/Tea Wastes for Cr(VI) Reduction and Removal

Waste tea and coffee dusts were used as biomaterials for the reduction and adsorption of Cr(VI). The total Cr ions in the solution and the Cr(VI) concentrations were measured to determine the percentage conversion and adsorption of Cr (VI) ions.

4.4.1 Effect of pH

It is well known that besides various physicochemical effects, pH is an important variable in the ion exchange governed adsorption processes, by which surface charges may be changed or modified.

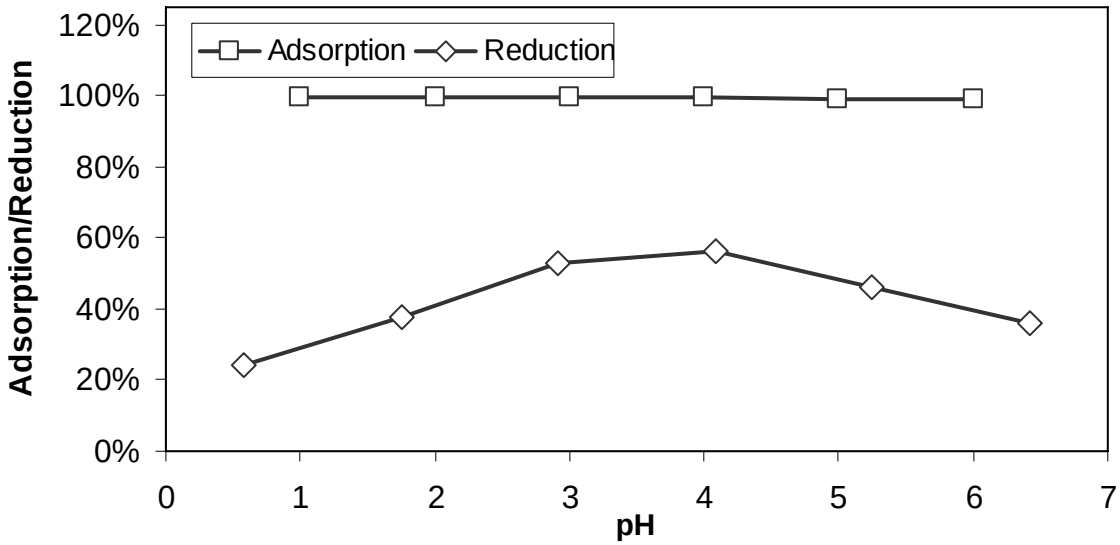

Figure 4.21
pH Optimization for Adsorption/Reduction of Cr(VI) by Tea Dust

In order to observe the influence of this parameter on the adsorption, tea and cofee dusts were brought into contact with the Cr(VI) ions solutions for 6 h at different pH level, and the effect of pH on the metal uptake is summarised in Figure 4.22. Precipitation of Cr(III) ions are dominant at higher pH values, so all experiments were conducted at a pH lower than 8. Adsorption and reduction efficiency for tea and coffee dusts were analyzed, and the results are plotted in Figures 4.21 and 4.22. The optimum initial pH for reduction as well as adsorption was found to be 4.0. As illustrated in the figures, 100% of initial Cr(VI) ions were removed by 100% reduction and 60% adsorption from a solution of 25 mg L^{-1} by both dusts.

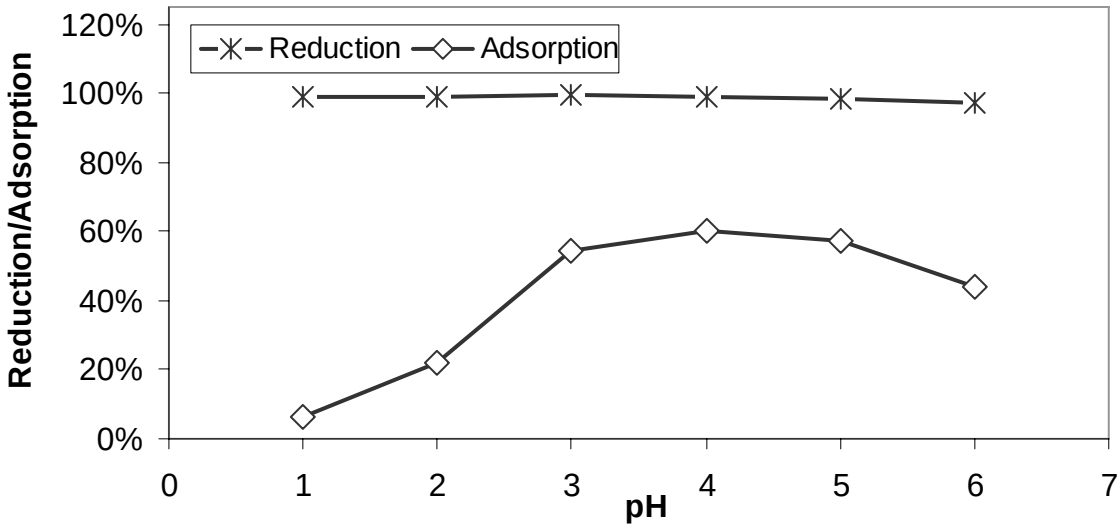

Figure 4.22
pH Optimization for Adsorption/Reduction of Cr(VI) by Coffee Dust

As can be seen from the figure the optimum pH for reduction as well as adsorption was found to be 4.0. 100% of Cr(VI) ions disappeared from the solution from all experimental solutions. The total Cr analysis results showed higer adsorption at pH 4 – 5 range, 60% of Cr ions were adsorbed from the solution containing 25 mg L^{-1} of Cr by both dusts.

4.4.2 Biosorbent Quantity Optimization

The biosorbent concentration has been found to be an important factor in the biosorption process. The influence of biosorbent dosage on percentage adsorption and Cr uptake is depicted in Figures 4.23 and 4.24.

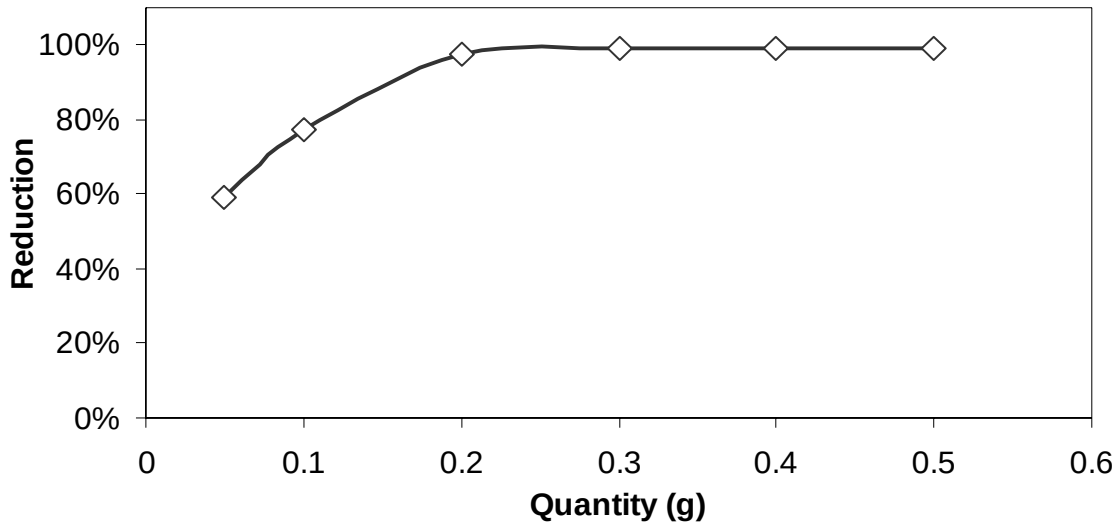

Figure 4.23
Effect of Biomass quantity for the Reduction/Adsorption of Cr (VI) ions by Tea Dust.

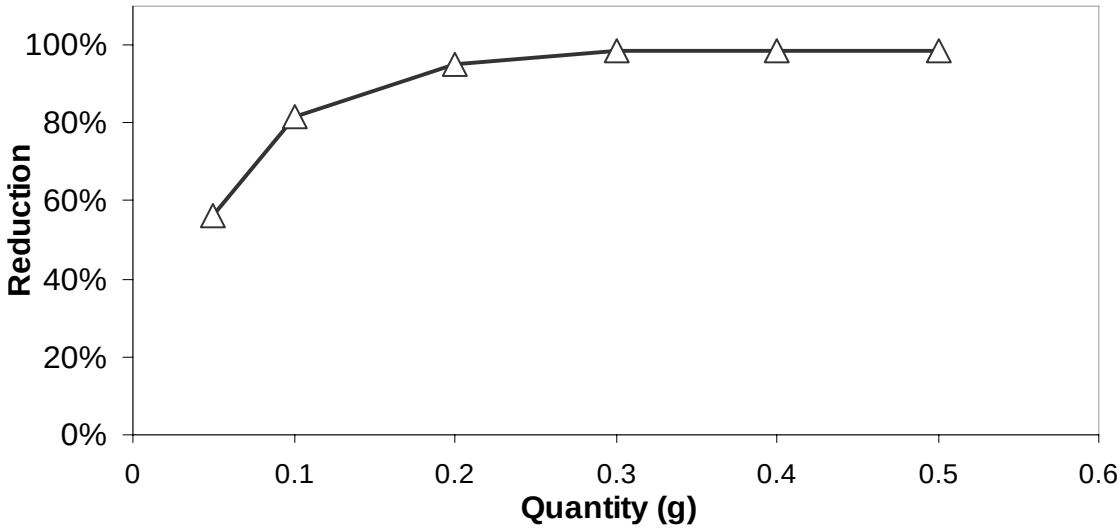

Figure 4.24
Effect of Biomass quantity for the Reduction/Adsorption of Cr (VI) ions by Coffee Dust

Biosorption studies were carried out using varying concentrations from 0.5 to 5 % (by wt.) of tea and coffee dust. The results showed that the increase in the sorbent dose from 0.5 to 3% resulted in increased Cr(VI) reduction rate (50% to 100%) of Cr(VI) ions. This is because of the availability of more binding sites for the complexation of Cr(VI) ions. An initial biomass

concentration of 3% (by wt) was found to be able to remove 100% of available Cr(VI) ions from 25 mg L^{-1} ionic solution. Further increment in sorbent dose over 3% (by wt) did not cause significant improvement in adsorption/reduction. This seems to be due to the binding of almost all the ions present in the solution to the sorbent and the establishment of equilibrium between the ions bound to the sorbent and the remaining unadsorbed in solution.

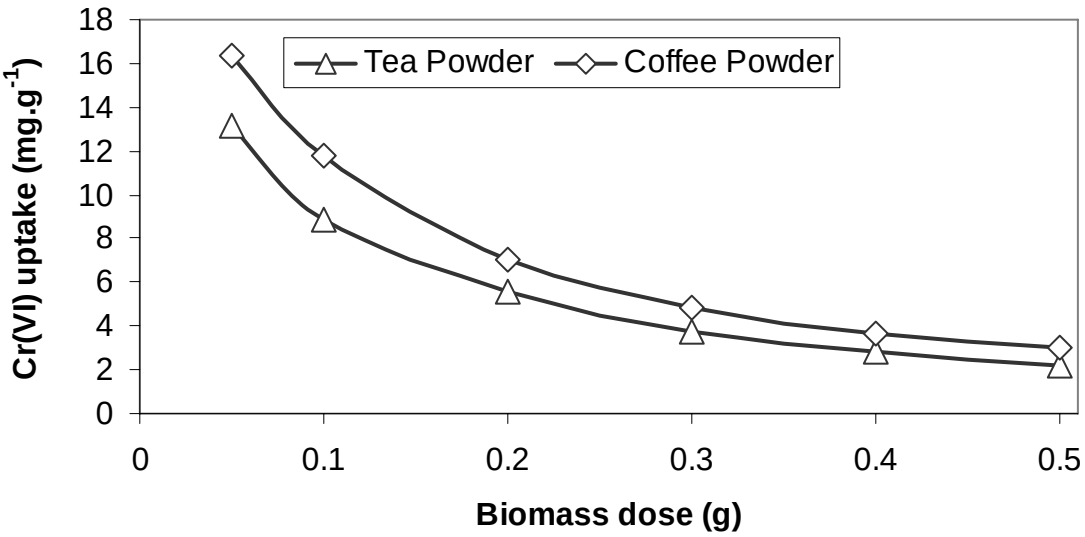

Figure 4.25
Effect of Adsorbent dose on uptake of Cr(VI) ions by Tea and Coffee Dust

However, Cr(VI) uptake values showed a reversible trend since it is a measure of the amount of Cr ions bound by unit weight of the biomass and therefore its magnitude decreased with the increase in biomass dose. Gadd and White (1989) explained this phenomenon by hypothesizing that an increase in biomass concentrations leads to interference between binding sites. Accordingly in the presence of high biomass concentration, there is a very rapid superficial adsorption onto the biosorbent and creates a lower metal concentration in solution than the conditions of lower sorbent density in the medium.

The concentration of both metal ions and the biosorbent are significant factors to be considered

in effective remediation. They determine the sorbent/sorbate equilibrium of the system. The optimum biosorbent dose required for the treatment of an effluent can therefore be determined on the basis of the concentration of contaminant metal ion and the volume of effluent to be treated. Orhan and Buyukgungor (1993) reported using 0.3 g of waste tea for the adsorption of Cr(VI), Cd(II), and Al(III) metal ions in batch studies containing 100 ml of metal solution.

4.4.3 Effect of Initial Metal Ion Concentration

The adsorption and reduction percentages determined at differential initial Cr(VI) concentrations for both tea and coffee dust are illustrated in Figure 4.26 and 4.27.

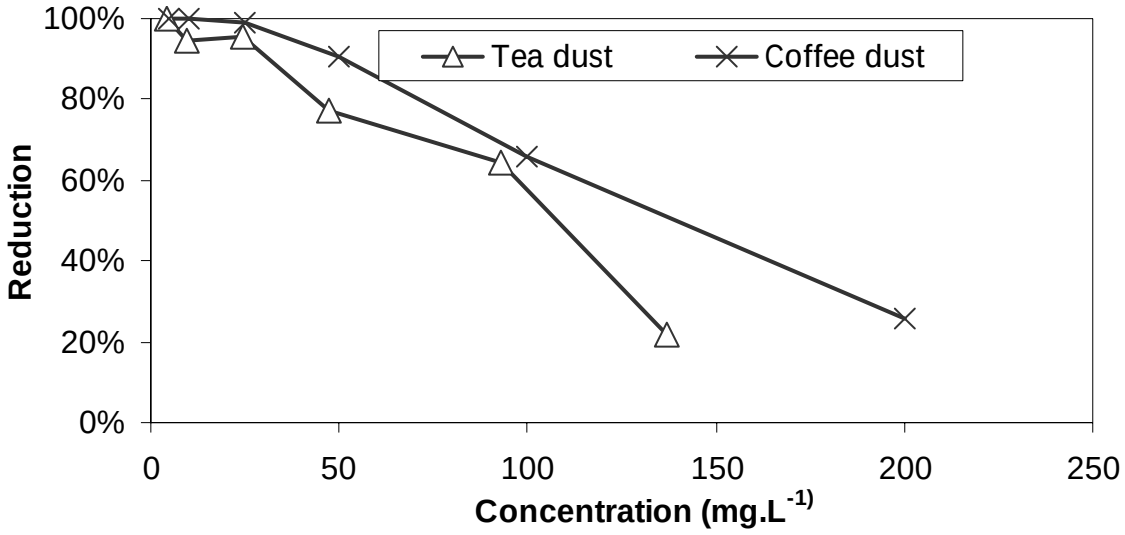

Figure 4.26
Effect of varying initial concentration of Cr(VI) for the Reduction by Tea Dust and Cofee Dust

Higher percentage reduction was observed in both biosorbents at lower initial concentrations (less than 25 ppm) but higher removal efficiency for adsorption was observed at 25 – 100 mg L^{-1}. The Cr(VI) uptake rate versus the residual Cr(VI) concentration are plotted in Fig 4.28. Consistent with other established adsorbents, the uptake rate increased for tea and coffee dust with the increase in the residual Cr(VI) concentration.

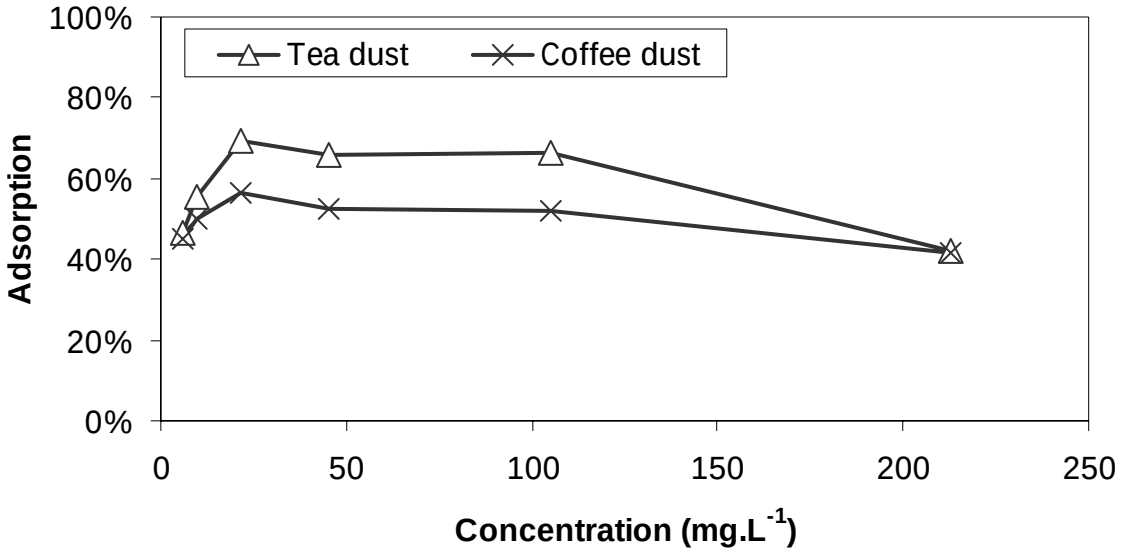

Figure 4.27
Effect of varying initial concentration of Cr(VI) for the Adsorption by Tea and Coffee Dust

However, the metal uptake capacity i.e. the quantity of metal adsorbed per unit weight of the sorbent displayed a reverse trend (Figure 4.28).

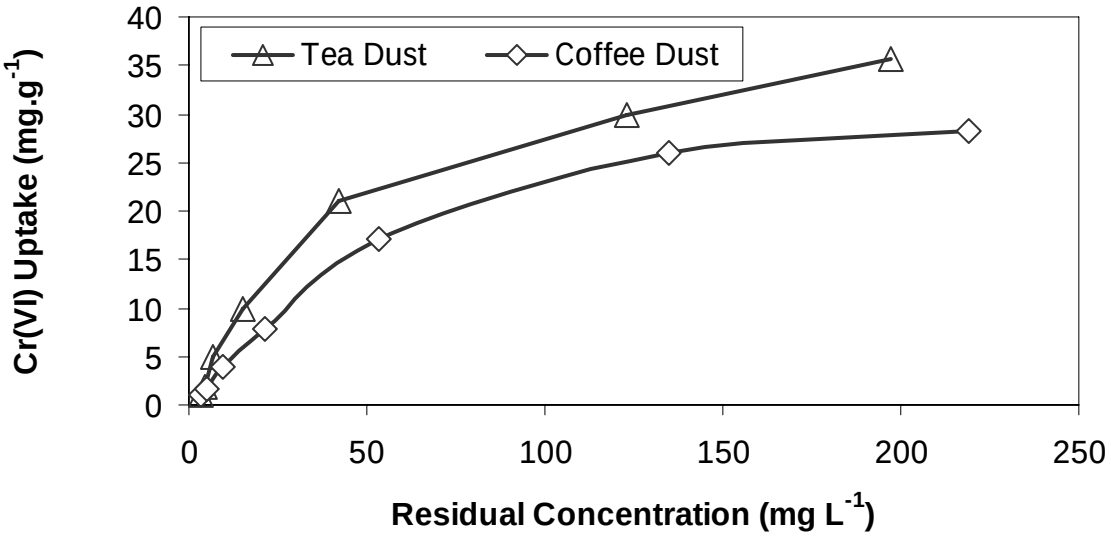

Figure 4.28
Comparison of Cr(VI) uptake capacities of Tea and Coffee dust at different initial concentration

The adsorption capacity (mg of Cr adsorbed per g of biosorbent) of both dusts was highest at 500 mg L^{-1} . The rate of adsorption is a function of initial concentration of ions. The reduction in the adsorption percentage at higher level concentration of Cr(VI) ions could be explained as follows. As the quantity of sorbent is kept uniform, the number of ions competing for the available sites on the biomass increases at higher initial concentrations of the sorbate. As a result of this, more ions are left unadsorbed in solution due to biosorbent saturation and the lack of binding sites for further complexation of Cr ions.

4.4.4 Metal Removal as a Function of Time

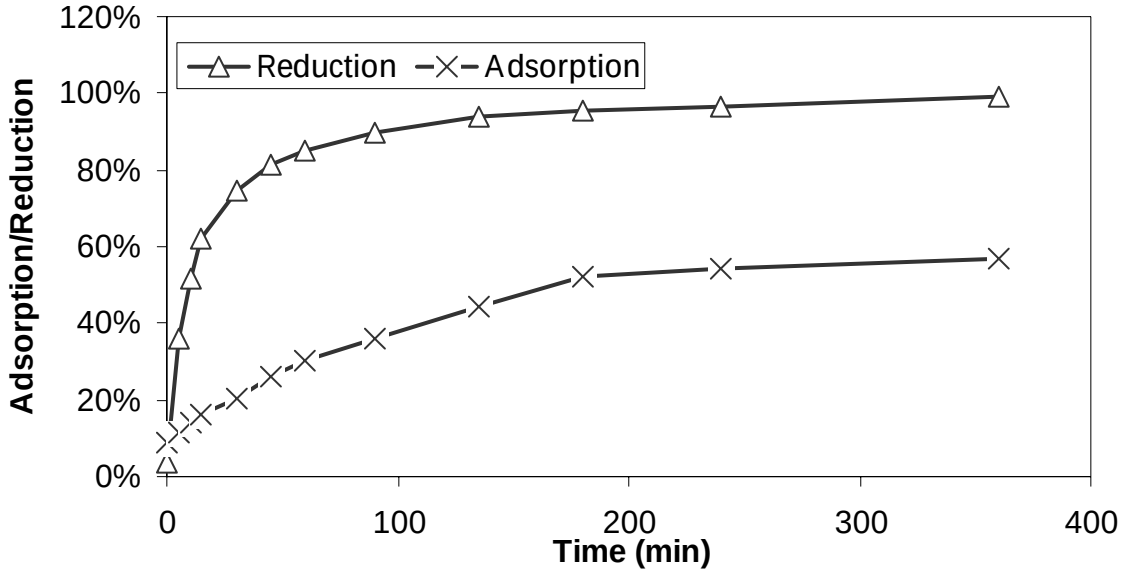

Figure 4.29
Kinetic study for the Reduction/Adsorption of Cr (VI) ions by Tea Dust

In order to determine the time required for the sorption equilibrium, experiments were carried out for six hours, and several samples were analyzed at regular intervals. As illustrated in Figure 4.29 and 4.30, the majority of the Cr(VI) ions was reduced by both tea and coffee dusts rapidly within 30 min of sorbent contact. As seen from the graph the adsorption of Cr was a slow process compared to the reduction and it took more than 3 hours to reach an equilibrium

for tea dust and more than 4 hours for coffee dust.

After three and four hours, the adsorption process by tea and coffee dusts respectively was very slow and almost attained equilibrium. However, both the dusts reduced more than 90% of the initial Cr(VI) within an hour and reached 100% reduction within 6 hours.

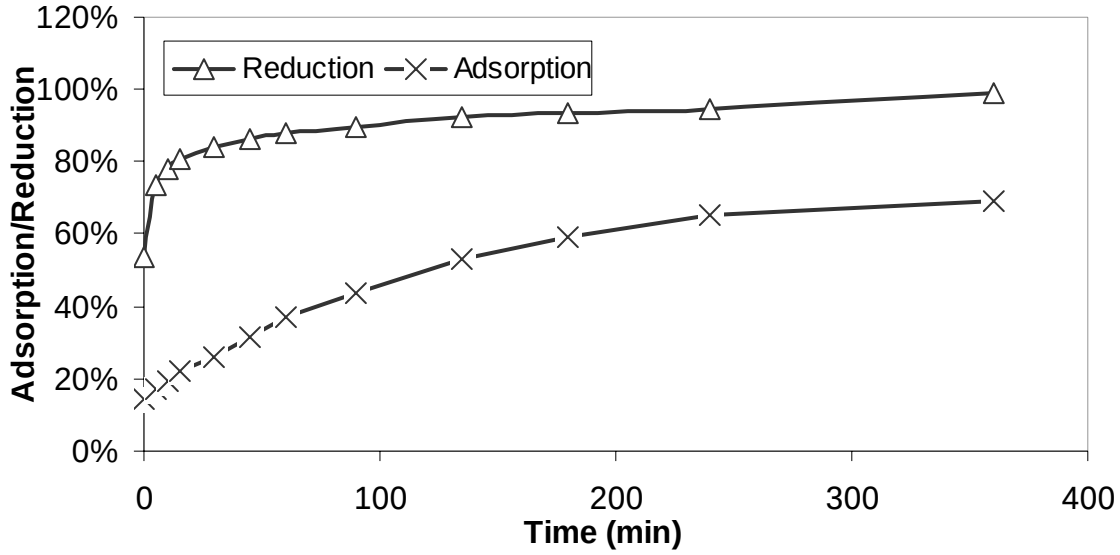

Figure 4.30
Kinetic study for the Reduction/Adsorption of Cr (VI) ions by Coffee Dust

Compared to tea dust, the coffee dust reduced Cr(VI) ions rapidly. More than 50% of Cr(VI) ions were instantaneously reduced when coffee dust was in contact with Cr(VI) solution (within 5 mins), compared to that of tea dust which reduced 30% of Cr(VI) ions within 5 minutes of contact. The coffee dust showed high adsorption percentage (almost 70%) compared to tea dust (less than 60%). For both the cases, most of the adsorption process happened within 3 hours of the contact with the biosorbent. This is because the kinetics of metal adsorption, which depends on physical adsorption onto cell surface is usually rapid during the early period of contact between the sorbent and the sorbate. The active adsorption

sites of the adsorbent got involved in Cr complexation as soon as the adsorbent is introduced into the system. So prolonged contact between the adsorbent and the adsorbate may not yield better adsorption since most of the adsorption process happened within few hours of time.

4.4.5 Adsorption Isotherms

The linearized isotherms were plotted by fitting the adsorption data into Langmuir and Freundlich adsorption isotherm models.

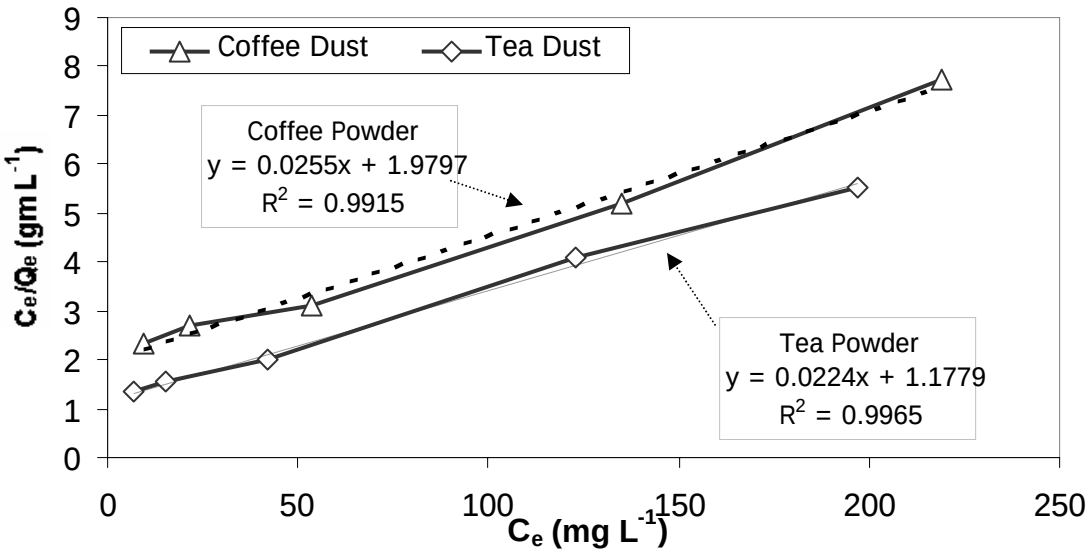

Figure 4.31
Langumir Adsorption Isotherm for Cr (VI) adsorption by Tea and Coffee Dust

The experimentally determined sorption isotherms over a concentration range of 5 - 500 mg L^{-1} Cr ions are presented in Figures 4.31 and 4.32. The steepness of the isotherm indicated the strength of affinity of the biosorbent for Cr(VI) ions. As depicted in Figure 4.31 the steepness of the isotherm curves for both dusts is almost the same (0.025 and 0.022), but the equilibrium concnetration for tea is low compared to that of coffee dust, thereby indicating a decreasing tendency of Cr adsorption potential for tea dust compared to coffee dust.

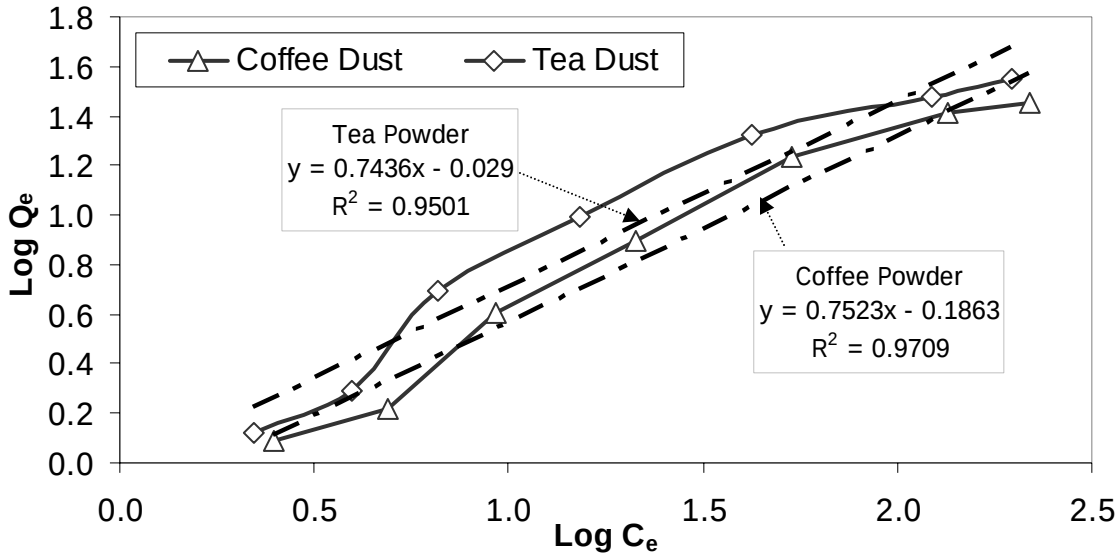

Figure 4.32
Adsorption Isotherm for Cr (VI) adsorption by Tea and Coffee Dust

The linearized Frendlich isotherms are plotted in Figure 4.32.This graph also shows the same trend as in Langumier isotherms, but the adsorption parameters are lower for coffee dust compared to the tea dust. The magnitude of Freundlich regression constants K_F (denoting adsorption capacity), 1/n (adsorption intensity), and correlation coefficient, and Langmuir isotherms Q_0 (maximum uptake) and K_L (energy of adsorption) and R^2 are given in Table 4.2

Table 4.2: Freundlich and Langmuir model isotherm constants for Cr(VI) adsorption for Tea and Coffee dust.
(Concentration range from 5 – 500 mg L^{-1} of Cr(VI) ions; adsorption pH = 4.0; biomass dose = 0.3 %, w/v; adsorption period = 6h)

	Freundlich Isotherm constants			**Langmuir Isotherms Constants**		
	K_F	n	R^2	Q_0 (mg g^{-1})	K_L	R^2
Sargassum	2.11	1.34	0.9	60.98	0.04	0.98
Ulva	0.34	1.16	1	36.1	0.01	0.97
Tea Dust	1.05	1.40	0.92	44.64	0.02	1.00
Coffee Dust	0.50	1.23	0.95	39.22	0.01	0.99

The affinity constants for all the biomaterials are close to 1. The maximum Cr uptake capacity

of waste tea and coffee dust was 44 and 39 mg g^{-1}, respectively, this is low compared to the uptake rate of *Sargassum* that is 60 mg g^{-1}. This was observed during the optimization of biosorbent dosage for tea and coffee dusts.

The optimum quantity for tea and coffee was 0.3 % (w/v) compared to 0.1 %(w/v) of *Sargassum* and *Ulva.* This means a higher quantity of waste tea and coffee dusts is required for removing equal amount of Cr(VI) ions from aqueous solutions. The adsorption as well as the reduction kinetics by coffee and tea dust gave attractive results compared to those of *Sargassum* and *Ulva.*

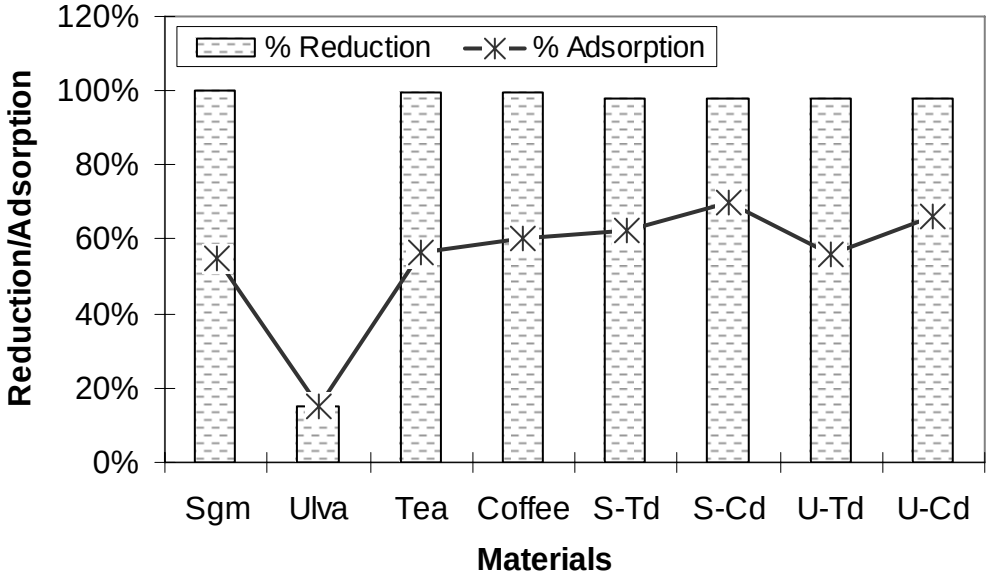

Figure 4.33
Percentage Reduction/Adsorption for Cr (VI) by different biomaterials
S-Td: *Sargassum* Tea dust; S-Cd: *Sargassum* Coffee dust*;* U-Td*: Ulva* Tea dust;
U-Cd: *Ulva* Coffee dust

The effective reduction and adsorption of Cr(VI) by using Sargassum, Ulva, Tea dust, Coffee dust, and Sargassum and Ulva in presence of Tea and Coffee dust were analyzed and are plotted in Figure 4.33. Used Coffee and Tea dusts showed adsorption capability that is comparable with *Sargassum* and *Ulva* for removing Cr(VI) ions from aqueous solutions, more

than 60% adsorption and 100% reduction. The overall adsoprtion as well as the reduction efficiency did not show any improvement by the presence of Tea or Coffee dust with *Sargassum*. However, the adsorption efficiency for *Ulva* tremendously improved while using together with Coffee and Tea dust.

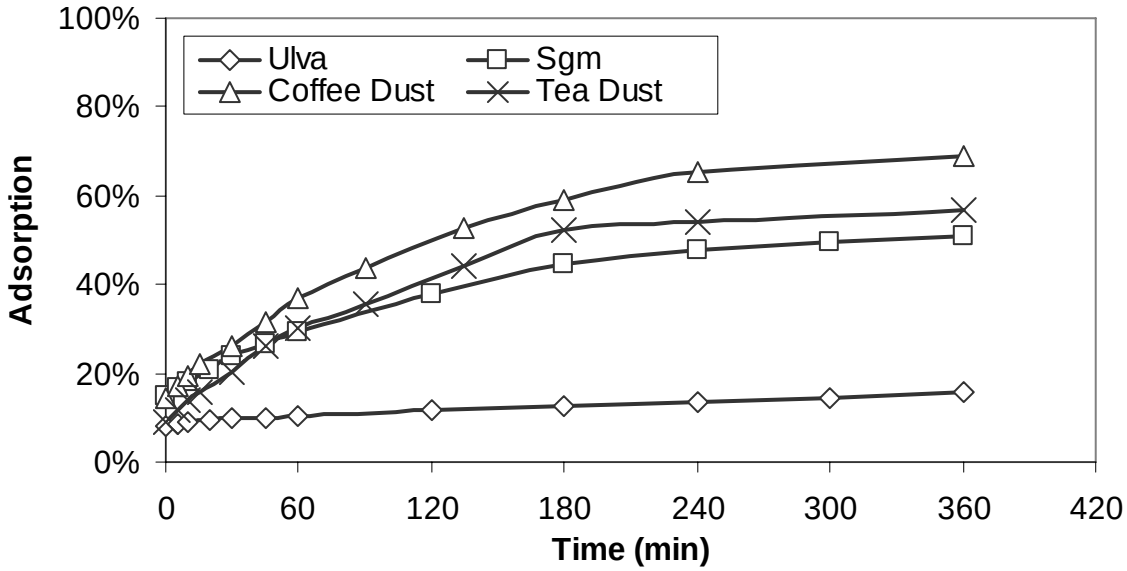

Figure 4.34
Percentage Adsorption for Cr (VI) by different biomaterials

The kinetic study results for these four biomaterials are plotted in Figure 4.34. By comparing these values plotted on this chart for the percentage adsorption of Cr(VI) by tea dust, coffee dust, *Sargassum, and Ulva*, it can be seen that used coffee and tea dusts showed better results compared to *Sargassum and Ulva*. The coffee dust adsorbed almost 70% of Cr ions while tea dust adsorbed almoct 60% of total Cr ions presented in the aqueous solution compared to 50% adsorption by *Sargassum* and less than 20% adsorption by *Ulva*.. Both biomaterials adsorbed more than 50% of the total Cr ions within 3 hours of contact with the solution. The kinetics of the reduction of Cr(VI) ions are plotted in Figure 4.35. Both biomaterials reduced more than 90% of available Cr(VI) ions within an hour of contact while *Sargassum* took more than 12

hours.

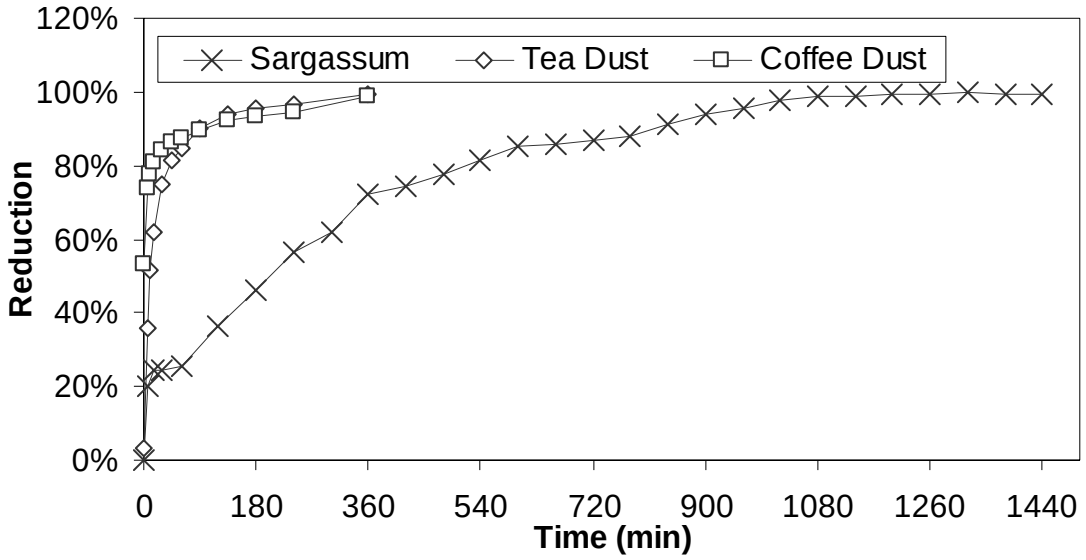

Figure 4.35
Percentage Reduction of Cr (VI) ions by *Sargassum*, used tea and coffee dust

Comparing the adsorption and reduction coefficients and efficiency, tea and coffee dusts show results similar to those with *Sargassum* while kinetics experiments proved that used coffee/tea dust is a better material for the effective removal of toxic Cr(VI) by adsorption and reduction. Both *Sargassum and Ulva* showed improvement in the adsorption and reduction of Cr(VI) ions by the addition of coffee and tea dust.

CHAPTER 5

CONCLUSION

This study reveals the important factors affecting biosorption of Cr ions by *Ulva* and *Sargassum* and other waste biomaterials such as waste tea and coffee dusts. Several experiments were carried out to study different adsorption parameters of *Ulva* compared to *Sargassum*. The major conclusions from these experiments are:

- *Ulva* was found to be less efficient in terms of adsorbing Cr ions from aqueous solutions.
- The removal of Cr (VI) ions by *Sargassum* biomass was a combination of reduction and adsorption.
- *Ulva* biomass was not able to reduce Cr(VI) in aqueous solution and hence a lower adsorption efficiency (<20%) compared to *Sargassum* (>60%).
- *Ulva* showed almost the same adsorption efficiency for removing Cr(III) ions from aqueous solution (~ 70%) compared to *Sargassum*.
- The formation of Cr(III) ions in the presence of *Ulva* was noticed to be low and hence the reduction process hinders the overall adsorption of Cr(VI) by *Ulva*.

Several pre-treatments followed by adsorption and kinetic experiments were carried out to investigate if there is any improvement in the adsorption characteristics and/or kinetics of *Sargassum* and *Ulva*. Chemicals such as acid, alkali, formaldehyde, and acetone were used for the pre-treatment and the adsorption of Cr(VI) and Cr(III) was studied. The major conclusions from these experiments are as follows:

- Pre-treatment by formaldehyde, acetone, and hydrochloric acid improved the adsorption capacity of *Sargassum* for Cr(VI) ions.
- Acetone-treatment improved the adsorption capacity of *Ulva* biomass for both Cr(VI) and Cr(III) ions. However, a negative trend on the adsorption efficiency of the pre-treated biomass was observed.
- There was no significant improvement in the total adsorption, or reduction of Cr(VI), or the adsorption of Cr(III) ions by the pre-treatment.
- The overall Cr uptake capacity (q – mg g^{-1} of biosorbent) was increased by the pre-treatment process. Acid modification increased the uptake capacity of *Sargassum* biomass for the removal of Cr(VI) (more than 200% increase in the Q value (140 compared to 60)). Pre-treatment of *Ulva* biomass by acetone provided better adsorption uptake rate (~ 200% (62 compared to 36). The pre-treatment improved the adsorption capacity in both biomasses.

The use of external reducing agents to reduce Cr(VI) ions to Cr(III) ions was investigated in order to improve the adsorption efficiency of *Ulva* biomass. 2.93 moles of ascorbic acid were able to reduce 1 mole of Cr(VI) ions instanstaneously. Several naturally occurring waste materials were used in this study for the reduction of Cr(VI) ions. The major conclusions from this study are as follows:

- Waste tea and coffee dusts were found to be effective in terms of reducing Cr(VI) to Cr(III) (upto 90% with an hour of exposure).
- Studies conducted using *Sargassum* and *Ulva* in the presence of these waste biomaterials indicated that the adsortion efficiency for both seaweeds was improved in

the presence of these materials.

- Used tea and coffee dusts also demonstrated their ability to adsorb Cr(VI) ions from the solution.
- Adsorption experiments were conducted using used tea and coffee dusts in order to optimize different adsorption parameters. Most of the influential parameters such as the effect of pH, the quantity of adsorbent, the initial metal ion concetration, and the kinetics were studied. The optimum pH was observed as pH 4, and the quantity was optimized as 0.3 % (wt/vol).
- Both tea and coffee dusts were able to adsorb 60% of the Cr species within 6 hours.
- Used Tea and Coffee dusts were found to be potential biomaterials for the effective removal of Cr from aqueous solutions.

Recommended Future Studies

Based on the exploratory research conducted in this project, the following studies are recommended in the context of removing heavy metals from contaminated water using low cost adsorbents.

1. Study the surface characteristics and properties of *Ulva fasciata* to understdand the difference in adsorption efficiency and capacity compared to those of *Sargassum* biomass.
2. Explore the possibilities of surface modification of *Ulva fasciata* biomass to enhance the adsorption efficiency so that Ulva biomass can alos be effectively utilized for the removal of heavy metals from aqueous solutions.
3. Extend this study to other heavy metals such as Arsenic, Lead, Copper etc. and to establish optimum adsorption parameters for used tea and coffee powder.
4. Conduct column studies and explore the possibilities of developing a pilot or even an industrial process unit for the effective removal of heavy metals from aqueous solutions using used tea and coffee powder.

References

Aderhold, D.; Wiliams,C.J.; Edyvean,R.G.J. 1996, "The removal of heavy metal ions by seaweeds and other derivatives", *Bioresource Technology* **58**, pp. 1-6.

Alkortak, I.; Hernandez, J.M.; Allica Becerril.; Amezaga. I.; Albizu. I. and Garbisu. C. 2004, "Recent findings on the phytoremediation of soils contaminated with environmentally toxic heavy metals and metalloids such as zinc, cadmium, lead, and arsenic", *Reviews in Environmental Science and Biotechnol,* **3**, pp. 71–90.

Anderson, L.D.; Kent, D.B.; Davis, J.A. 1994. "Batch experiments characterizing the reduction of Cr(VI) using suboxic material from a mildly reducing sand and gravel aquifer". *Environmental Science & Technology,* **28** (1), pp.178-185.

Anderson, R.A. 1997. "Chromium as an essential nutrient for humans", *Regulatory Toxicology and Pharmacology,* **26**, pp. S35-S41.

Arai,T.; Ikemoto.; Hokura, A.; Terada, Y.; Kunito, T.; Tanabe, S.; Nakai, I. 2004 "Chemical forms of mercury and cadmium accumulated in marine mammals and seabirds as determined by XAFS analysis", *Environmental Science & Technology*, **8**, pp. 6468–6474.

Ashkenazy, R.; Gottlieb,L.; Yanni, S. 1997, "Characterization of acetone-washed yeast biomass functional groups involved in lead biosorption", *Biotechnology and Bioengineering*, **55**, pp. 1-10.

Avery, A.V.; Tobin, J.M. 1992, "Mechanisms of strontium uptake by laboratory and brewing strains of Saccharomyces cerevisiae", *Applied Environmental Microbiology*, **58**, pp. 3883–3889.

Baral, A.; Engelken, R.D. 2002. "Chromium-based regulations and greening in metal finishing industries in the USA". *Environmental Science and Pollution Reasearch*, **5**, pp. 121-133.

Barnhart, J. 1997. “Occurrences, uses and properties of chromium”. *Regulatory Toxicology and Pharmacology*. **26**, S3-S7.

Beiley, S.E.; Olin, T.J.; Bricka, R.M.; Adrian, D.D. 1999, “A review of potentially low-cost sorbents for heavy metals”, *Water Research*, **33**, pp. 2469-2479.

Çay, S.; Uyanık, A.; Oza, A.; Ozark. 2004, “Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste”, *Separation and Purification Technology*, **38** (3), pp. 273-280.

Chan, C.F.; Glazer, A.N.; West, J.A. 1997, “An unusual phycocyanobilin-containing phycoerythrin of several bluish-colored, acrochaetioid, freshwater red algal species”, *Journal of Phycology,* **33** (4), pp. 617-624.

Chang, J.S.; Law, R.; Chung, C.C. 1997, “Biosorption of lead, copper and cadmium by biomass of Pseudomonas aeruginosa PU21”, *Water Research*, **31**, pp. 1651-1658,

Chapman, V.J. 1980, *Seaweeds and their uses*. London, UK, Chapman & Hall, pp. 334.

Costa, M. 2003. “Potential hazard of hexavalent chromate in our drinking water”. *Toxicology Applied Pharmacology*, **188**, pp.1-5.

Cushine, Jr, G.C. 1985. “*Electroplating wastewater pollution control technology*”, Noyes publications, 152-219

Davis, T.A.; Volesky, B.; Mucci, A. 2003, “A review of the biochemistry of heavy metal biosorption by brown algae”, *Water Research*, **37**(18), pp. 4311-4330.

Deepa, K.K.; Sathish, K.M.; Binupriya, A.R.; Murugesan, G.S.;.Swaminathan, K.;.Yun, S.E. 2006, "Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of Aspergillus flavus", *Chemosphere,* **62**(5), pp. 833-840.

Dinesh, M.; Kunwar, P.S.; Vinod, K.S. 2006, "Reply to "comments on the removal mechanism of Hexavalent Chromium by biomaterials or Bio-material based activated carbons", *Industrial and Engineering Chemistry Research*, **45**, pp. 2411-2412.

Environmental Protection Agency, Cosumer fact sheet on chromium. http://www.epa.gov/safewater/contaminants/dw_contamfs/chromium.html

Evans, M.N.; Chirwa.; Wang, Y.T. 1997, "Hexavalent Chromium Reduction by Bacillus sp. in a Packed-Bed Bioreactor", *Environmental Science & Technology*, **37**, pp. 1446-1451.

Farhoosh Reza *, Gholam A. Golmovahhed, Mohammad H.H. Khodaparast. 2007, "Antioxidant activity of various extracts of old tea leaves and black tea wastes (*Camellia sinensis L.*)". *Food Chemistry*, **100**, pp 231–236

Feng, D.; Aldrich, C. 2004. "Adsorption of Heavy Metals by Biomaterials Derived from the Marine Algae Ecklonia maxima", *Hydrometallurgy*, **73**(1-2), pp.1-10.

Fourest, E.; Volesky, B. 1996, "Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of Sargassum fluitans", *Environmental Science & Technology* 30 (1): 277-282.

Fourest. E.; Roux, J.C. 1992, "Heavy-metal biosorption by fungal mycelial by-products - mechanisms and influence of pH", *Applied Microbiology and Biotechnology,* **37**(3), pp. 399-403.

Gadd, M.G.; Christopher, W. 1989, "Uptake and intracellular compartmentation of thorium in saccharomyces cerevisiae", *Environmental Pollution*, **61**(3), pp. 187-197.

Gardea, T.J.L.; Tiemann, K.J.; Armendariz, V.; Bess, O.L.; Chianelli, R.R.; Rios, J; Parsons, J.G.; Gamez, G. 2000, "Characterization of Cr(VI) binding and reduction to Cr(III) by the agricultural byproducts of Avena monida (oat) biomass", *Journal of Hazardous Materials*, **80**, pp 175.

Gong, R.M.; Ding, Y.; Liu, H.J. 2005, "Lead biosorption and desorption by intact and pretreated spirulina maxima biomass", *Chemospehre,* **58**(1), pp. 125-130.

Holan, Z.R.; Volesky, B. 1995, "Biosorption of heavy-metals", *Biotechnology Progress* **11**(3), pp. 235-250.

Jalali, R.H.; Ghafourian; Asef, Y.; Davarpanah, S.J.; Sepehr, S. 2002, "Removal and recovery of lead using nonliving biomass of marine algae", *Journal of Hazardous Materials*, **92,** pp. 253–262.

Hunt, J. P.*" Metal ions in aqueous solution"*; W. A. Benjamin, Inc.: New York, 1965; pp 45-55

Kapoor, A.; Viraraghavan, T. 1995, "Fungi biosorption - an alternative treatment option for heavy metal bearing wastewaters: a review", *Bioresource Technology*, **53,** pp. 195–206.

Kapoor, A.; Viraraghavan, T.; Cullimore, D.R. 1999, "Removal of heavy metals using the fungus Aspergillus niger", *Bioresource Technology,* **70** (1),pp. 95-104.

Karthikeyan, S.; Balasubramanian, R.; Iyer, C.S.P. 2006, "Evaluation of the marine algae Ulvafasciata and Sargassum sp. for the biosorption of Cu(II) from aqueous solutions", *Bioresource Technology,* In press.

Kim, Y.W.; Park, J.Y.; Yoo, Y.T.J. 1995, *Abstract Papers American Chemical Soceity*, **209**, Meet.,Pt.1, BIOT 101.

Kratochvil, D.; Patricia, P.; Volesky, B. 1998, "Removal of Trivalent and Hexavalent Chromium by Seaweed Biosorbent", *Environmental Science & Technology*, **32**, pp. 2693-2698.

Kurniawan, T.A.; Chan, G.Y.S.; Low, H.; Babel, S. 2006. Physicochemical treatment techniques for wastewater laden with heavy metals, *Chemical Engineering Journal,* **118**, pp. 83–98.

Kuyucak, N.; Volesky, B. 1989, "The mechanism of cobalt biosorption", *Biotechnology and Bioengineering*, **33** (7): pp. 823-831.

Lacher, C.; Smith, W.R. 2002, "Sorption of Hg(II) by Potamogeton natans dead biomass", *Minerals Engineering*, **15** (3),pp. 187-191.

Lahaye, M.; Axelos, M. 1993, "Gelling properties of water-soluble polysaccharides from proliferating marine green seaweeds (ulva spp.)", *Carbohydrate polymers,* **22** (4), pp. 261-265.

Lee, D.C.; Park, C.J.; Yang, J.E.; Jeong, Y.H.; Rhee, H.I. 2000, "Screening of hexavalent chromium biosorbent from marine algae", *Applied Microbiology and Biotechnolgy*, **54**, pp. 445–448.

Livenspil O, *Chemical Reaction Engineering*, 3rd Edition, John Wiley & Sons.

Metcalf and Eddy. 2005, *Wastewater Engineering Treatment Disposal and Reuse*. 4th Edition. McGraw Hill.

Morand, P.; Birand, X. 1996, "Excessive growth of macroalgae: a symptom of environmental disturbance", *Botanica Marina*, **39**, pp. 491–516.

Muraleedharan, T.R.; Ligy, P.; Iyengar, L.; Venkobachar, C. 1994, "Application studies of biosorption for monazite processing industry effluents"**,** *Bioresource Technology,* **49**(2), pp. 179-186.

National Environmental Agency
http://app.nea.gov.sg/cms/htdocs/article.asp?pid=1644

Orhan, Y.; Buyukgungor, H. 1993**, "**The removal of heavy metals by using agricultural wastes", *Water Science and Technology*, **28**(2), pp. 247-255.

Pangnelli, F.; Birand, X. 1996. "Excessive growth of macroalgae: a symptom of environmental disturbance", *Botanica Marina*, **39**, pp. 491-516.

Park, D.; Yun, Y.S.; Park, J.M. 2004, "Reduction of hexavalent chromium with the brown seaweed Ecklonia biomass", *Environmental Science and Technology,* **38**, pp. 4860–4864.

Park, D.; Yun, Y.S.; Park, J.M. 2005, "Studies on hexavalent chromium biosorption by chemically-treated biomass of Ecklonia sp., *Chemosphere*, **60**, pp. 1356-1364.

Park D.; Yun, Y.S.; Yim, K.H.; Park, J.M. 2006a, "Effect of Ni(II) on the reduction of Cr(VI) by Ecklonia biomass", *Bioresource Technology,* **97** (14), pp. 1592-1598.

Park, D.; Yun, Y.S.; Park, J.M. 2006b, "Comment on the Removal Mechanism of Hexavalent Chromium by Biomaterials or Biomaterial-Based Activated Carbons", *Journal of Hazardous Materials*, in press.

Park, D.; Yun, Y.S.; Park, J.M. 2006c, "Removal Mechanism of Hexavalent Chromium by Biomaterials or Biomaterial-Based Activated Carbons", *Journal of Hazardous Materials*, in press

Paterson, J.W. 1985, *Industrial Wastewater Treatment Technology* (2nd edn.), Butterworth-Heinemann, London.

Pauline, A.B.; Joseph, M.B.; Stephen, J.A. 2001, "The application of kudzu as a medium for the adsorption of heavy metals from dilute aqueous wastestreams", *Bioresource Technology*, **78**, pp. 195-201.

Percival, E.; McDowell, R.H. 1967, *Chemistry and Enzymology of Marine Algal Polyssacharides*, Academic Press, London (1967), pp. 117.

Sheng, P.X.; Tan, L.H.; Chen, P.J.; Ting, Y.P. 2004, "Biosorption Performance of Two Brown Marine Algae for Removal of Chromium and Cadmium", *Journal of Dispersion Science and Technology*, **25**(5), pp. 679-686.

Raji, C.; Anirudhan, T.S. 1998, "Batch Cr(VI) removal by polyacrylamide-grafted sawdust - Kinetics and thermodynamics", *Water Research*, **32**(12), pp. 3772-3780.

Ramos, K.S.; Bowes, R.C.; Ou, X.l. 1994, "Responses of vascular smooth muscle cells to toxic insult cellular and molecular perspectives for environmental toxicants", *Journal of Toxicology and Environmental Health*, **43**(4), pp. 419-440.

Rollinson, C.L. 1973, *In comprehensive Inorganic Chemistry* – 3rd Ed., Trotman Dickenson,Pergamon Press Ltd. Oxford, pp. 691 – 694.

Ruthuven, D.M. 1992, *Principles of Adsorption and Adsorption Processes*, John Wiley.

Schiewer, S.; Volesky, B. 1995, "Modeling of the proton-metal ion-exchange in biosorption", *Environmental Science & Technology*, **29**(12), pp. 3049-3058.

Schiewer, S.; Wong, M.H. 1999, "Metal Binding Stoichiometry and Isotherm Choice in Biosorption", *Environmental Science & Technology,* **33** (21), pp. 3821 -3828.

Schiewer, S.; Wong, M. H. 2000, "Ionic strength effects in biosorption of metals by marine algae", *Chemosphere,* **41**(1-2), pp. 271-282.

Schuurman, G.; Market, B. 1997, *Trace metals, in Ecotoxicology, Ecological fundamentals, chemica exposure and biological effects*, John Wiley & Sons, New-York, 7: 167-184.

Siegel, B.Z.; Siegel, S.M. 1973, "The chemical composition of algal cell walls", *Critical Reviews in Microbiology*, **3**(1), pp.1-26.

Simmons, P.; Singleton, I. 1996, "A method to increase silver biosorption by an industrial strain of Saccharomyces cerevisiae", *Applied Microbiology and Biotechnology*, **45**, pp. 278–285.

Stumm,W.; Morgen, J.J. *Aquatic Chemistry*, 3rd Edition, John Wiley & Sons. 1996.

Susan, E.; Bailey.; Trudy, J.; Olin, R.; Bricka, M.; Adrian, D.D. 1999, "A Review of potentially low-cost sorbents for heavy metals", *Water Research,* **33**(11), pp. 2469 – 2479.

Suzuki, Y.; Kametani, T.; Maruyama, T. 2005, "Removal of heavy metals from aqueous solution by nonliving Ulva seaweed as biosorbent", *Water Research,* **39**, pp. 1803–1808

Tee, T.W.; Khan, A.R.M. 1988, "Removal of lead, cadmium and zinc by waste tea leaves", *Environmental Technology Letters*, **9**(11), pp. 1223-1232.

Ting, Y.P.; Teo, W.K. 1994, "Uptake of cadmium and zinc by yeast: Effects of co-metal ion and physical/chemical treatments" , *Bioresource Technology*, **50**(2), pp. 113-117.

Torresdey, G.; Tiemann, J. L.; Armendariz, K. J.; Bess, O.V.; Chianelli, L.; Rios, R.R.; Parsons, J.; Gamez, J.G. 2000, "Characterization of Cr(VI) binding and reduction to Cr(III) by

the agricultural byproducts of Avena monida (oat) biomass", *Journal of Hazardous Material*, **80**, pp. 175.

US EPA Method 7196: http://www.epa.gov/sw-846/pdfs/7196a.pdf#search=%22US%20EPA%20method%207196%22

Valiela, J.; McClelland, J.; Hauxwell, P.J.; Behr. D.; Hersh.; Foreman, K. 1997, "Macroalgal blooms in shallow estuaries: controls and ecophysiological and ecosystem consequences", *Limnology and Oceanography,* **42**, pp. 1105–1118.

Veglio, F.; Beolchini, F. 1997, "Removal of metals by biosorption: a review", *Hydrometallurgy*, **44**, pp. 301–316.

Volesky, B.; Prasetyo, I. 1994, "Cadmium removal in a biosorption column", *Biotechnology and Bioengineering*, **43**(11), pp. 1010-1015.

Volesky, B. 1990a, "Biosorption and Biosorbents", *Biosorption of Heavy Metals*, CRC press, Florida, pp. 3–5.

Volesky, B. 1990b, "Biosorption by fungal biomass", *Biosorption of heavy metals*, CRC press, Florida, pp. 140–171.

Volesky, B. 2001, "Detoxification of metal-bearing effluents: biosorption for the next century", *Hydrometallurgy*, **59**(2-3), pp. 203-216.

Volesky, B. 2003a, *Sorption and Biosorption*, BV- Sorbex Inc., St. Lambert, Quebec, Canada, pp. 316.

Volesky, B. 2003b, *Sorption and Biosorption*, BV Sorbex, Inc, 2003. pg 88-89.

Wang, J.; Chen, C. 2006, “Biosorption of heavy metals by Saccharomyces cerevisiae: A review”, *Biotechnology Advances,* **24**, pp. 427-451.

Williams, C.J.; Anderhold, D.; Edyvean, G.J. 1996, “Comparison betweeen Biosorbents for the removal of metal ions from aqueous solutions”, *Water Reasearch*, **32**, pp. 216-224.

Wittbrodt, P.R.; Palmer, C.D. 1996, “Effect of temperature, ionic strength, background electrolytes, and Fe(III) on the reduction of hexavalent chromium by soil humic substances”, *Environmental Science & Technology* **30**(8), pp. 2470-2477.

Xie, J.Z.; Chang, H.L.; Kilbane,J.J. 1996, “Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents”, *Bioresource Technology*, **57**, pp. 127-136.

Zemke, W.L.; Ohno, M.J. 1999, “World seaweed utilization: an end-of-century summary”, *Journal of Applied Phycology*, **11**, pp. 369–376.